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U.S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 12 FEBRUARY 1934 No. 2

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BUREAU OF STANDARDS JOURNAL OF RESEARCH

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RESEARCH PAPER RP639

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

A METHOD OF ADJUSTING THE TEMPERATURE COEFFICIENT AND RESISTANCE OF LOW-VALUED RESISTANCE STANDARDS

By Frank Wenner and James L. Thomas

ABSTRACT

It is shown (1) that the temperature coefficient of low-valued resistance standards, which are of the 4-terminal type, may be either larger or smaller than the temperature coefficient of the resistance material used in their construction; (2) that in many cases it is possible to adjust the temperature coefficient to a practically zero value at a selected temperature; and (3) that the resistance may be decreased without the addition of a shunt, and without disturbing brazed connections between the resistance material and the copper terminals.

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I. INTRODUCTION

Low-valued resistance standards not infrequently have temperature coefficients differing considerably from that of the resistance material used in their construction. Such standards are of the 4-terminal type and the resistance element usually consists of two or more manganin wires in parallel or one or more manganin sheets in parallel. These wires or sheets are generally brazed to copper terminal posts and, since the copper has a relatively high temperature coefficient, it has generally been considered advisable to attach the potential connections in such a manner as to include a minimum amount of copper resistance between them. In fact, in many cases the potential connections are made directly on the manganin.

It is the purpose of this paper to point out, in case of an unsymmetrical construction: (1) that even with the potential connections made directly on the manganin, the copper terminals may be a factor affecting the temperature coefficient of the resistance standard; (2) that with the potential connections on the manganin the temperature coefficient may be changed by changing the section of the copper current posts; (3) that with the potential connections made on the copper current posts the temperature coefficient of the resistance standard may be either greater or less than the temperature coefficient of the manganin; (4) that with the potential connections on the copper current posts, the temperature coefficient and resistance may

be changed by changing the position of the potential connections or the section of the current posts, or both; (5) that there is a fairly definite relation between the change in temperature coefficient of a resistance standard, the temperature coefficient of the copper current posts and the change in resistance of the standard brought about by either a change of the section of the current posts or movement of the potential connections to other points on the current posts. More specifically, when the temperature coefficient is changed in this way, the magnitude and the direction of the change may be calculated from the temperature coefficient of the current posts and the observed change of the resistance; (6) that lowering the points of attachment of the potential connections on the current posts or a reduction of the sections of the current posts below the upper manganin wire or upper edge of the manganin sheet or sheets and above the points of attachment of the potential connections lowers the resistance and the temperature coefficient while a reduction of the section of the resistance material increases the resistance without materially changing the temperature coefficient; and (7) that changing the temperature coefficient by changing points of attachment of the potential connections or sections of current posts has no material effect on the load coefficient.

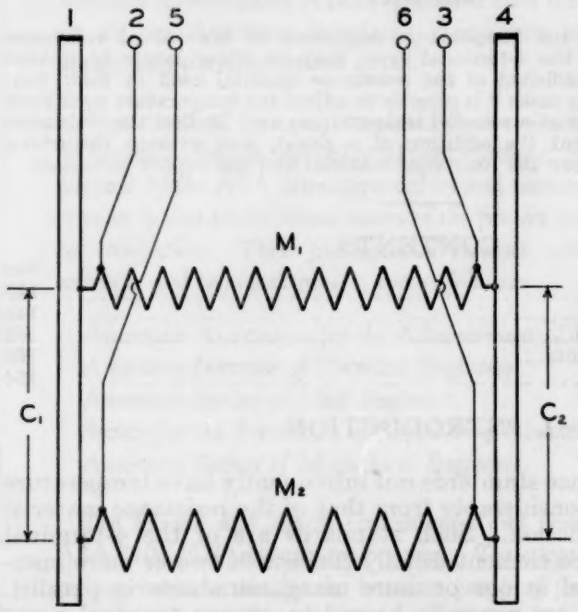

FIGURE 1.—*Resistance standard with two sets of potential terminals.*

Here 1 and 4 are current terminals, 2 and 3 are one and 5 and 6 are another set of potential terminals, M_1 and M_2 are the resistances of two manganin wires connected in parallel, and C_1 and C_2 are the resistances of the parts of the copper current posts between the manganin wires. Since the temperature coefficient of C_1 and C_2 is high relative to that of M_1 and M_2 a change in temperature causes a change in the current distribution between M_1 and M_2. Therefore not only the resistance but also the temperature coefficient depends on which set of potential terminals is used

II. THEORY

That the copper terminals may affect the temperature coefficient of low-valued 4-terminal resistance standards even when the potential terminals are connected directly to the manganin may be seen by considering the arrangement shown in figure 1. The essential parts are 2 manganin wires, shown as resistances; 2 current posts, and 4 potential leads. Here 1 and 4 are current terminals, 2 and 3 are one set of potential terminals, and 5 and 6 are another set of potential terminals, giving in effect two 4-terminal resistances which will be designated R_{1234} and R_{1564}. Let M_1 be the resistance of the upper and M_2 be the resistance of the lower branch, each considered for the

present as made up entirely of manganin, and C_1 and C_2 be the resistances of the parts of the current posts between the manganin wires. Then if I is the current entering through terminal 1 and leaving through terminal 4, I_1 is the current in the upper and I_2 is the current in the lower manganin wire, it is easily seen that

$$\frac{I_1}{I}=\frac{M_2+C_1+C_2}{M_1+M_2+C_1+C_2} \tag{1}$$

and

$$\frac{I_2}{I}=\frac{M_1}{M_1+M_2+C_1+C_2} \tag{2}$$

Since the proportional change of C_1 and C_2 with temperature is large in comparison with that of the manganin, if M_1 and M_2 change the same proportional amount for the same change in temperature, $\frac{I_1}{I}$ increases with an increase of the temperature and $\frac{I_2}{I}$ decreases with an increase of the temperature. Consequently, if 2 and 3 are used as potential terminals, the proportional increase of the ratio of the potential drop to the current I, which is the 4-terminal resistance R_{1234}, is greater than the proportional increase of M_1 or M_2. Likewise, if 5 and 6 are used as potential terminals, the proportional increase of the 4-terminal resistance R_{1564}, with temperature, is less than the proportional increase of M_1 or M_2. Incidentally whether or not the individual temperature coefficients of M_1 and M_2 are equal, the rate of increase of R_{1234}, with temperature, will be greater than that of R_{1564}. Obviously, if the section of either current post between the upper and lower wires were reduced, this would increase the difference in the rate of change of R_{1234} and R_{1564}, with temperature.

If the potential connections 2 and 3 are made on the copper current posts at points opposite to the points of attachment of the upper manganin wire, the resistance

$$R_{1234}=\frac{M_1\ (M_2+C_1+C_2)}{M_1+M_2+C_1+C_2} \tag{3}$$

If the potential connections 5 and 6 are made on the copper current posts at points opposite the point of attachment of the lower manganin wire, the resistance

$$R_{1564}=\frac{M_2M_1}{M_1+M_2+C_1+C_2} \tag{4}$$

That there is of necessity some brazing material—and usually some copper resistance—in each branch follows from the fact that the three-way electrical junctions between the wires and upper and lower ends of the current posts cannot be considered as points but must be considered as surfaces. These surfaces may or may not intersect boundaries between the manganin and brazing material, but never quite coincide with them nor in effect lie entirely within the manganin.

Each branch, therefore, contains some brazing material and usually some copper but not necessarily all of a manganin wire. Let D_1 be the contribution of the brazing material and copper, and M_1' be limited to the contribution of the manganin to the resistance of the upper branch. Also let D_2 and M_2' apply in like manner to the lower branch. Further let $D \equiv (D_1 + D_2)/2$, $M \equiv (M_1' + M_2')/2$ and $C \equiv (C_1 + C_2)/2$. If then M_1' and M_2' are nearly equal, and both C and D are small in comparison with M, neglecting second and higher order terms, it follows that the resistance

$$R_{1234} = \frac{M}{2} + \frac{D}{2} + \frac{C}{2} \tag{5}$$

and the resistance

$$R_{1564} = \frac{M}{2} + \frac{D}{2} - \frac{C}{2} \tag{6}$$

Similar approximate solutions for n wires of nearly equal resistance uniformly spaced along the current posts between points of attachment of the potential connections, are

$$R_{1234} = \frac{M}{n} + \frac{D}{n} + \frac{(2n-1)C}{3n} \tag{7}$$

and

$$R_{1564} = \frac{M}{n} + \frac{D}{n} - \frac{(n+1)C}{3n} \tag{8}$$

If M, C, and D apply at a particular temperature, 25 C for example at some other temperature t

$$R_{1234} = \frac{M}{n}[1 + \alpha(t-25) + \beta(t-25)^2] + \frac{D}{n}[1 + \delta(t-25)] + \frac{(2n-1)C}{3n}[1 + \gamma(t-25)] \tag{9}$$

and

$$R_{1564} = \frac{M}{n}[1 + \alpha(t-25) + \beta(t-25)^2] + \frac{D}{n}[1 + \delta(t-25)] - \frac{(n+1)C}{3n}[1 + \gamma(t-25)] \tag{10}$$

Here α and β are the averages of the temperature coefficients of the manganin wires, γ is the temperature coefficient of the copper current posts, and δ is the weighted average of the temperature coefficients of the brazing material and copper resistances in the branches, all applying with a reference temperature of 25 C. If additional second and higher order terms are neglected

$$R_{1234} = N\left[1 + \frac{D}{nN} + \frac{(2n-1)C}{3nN} + \alpha(t-25) + \beta(t-25)^2 + \frac{D}{nN}\delta(t-25) + \frac{2n-1}{3nN}C\gamma(t-25)\right] \tag{11}$$

and

$$R_{1564}=N\left[1+\frac{D}{nN}-\frac{(n+1)C}{3nN}+\alpha(t-25)+\beta(t-25)^2\right.$$
$$\left.+\frac{D}{nN}\delta(t-25)-\frac{n+1}{3nN}C\gamma(t-25)\right] \quad (12)$$

where N is the average resistance of the wires divided by the number. It will be seen that the temperature coefficient of R_{1234} is larger than the temperature coefficient of R_{1564} by $\gamma C/N$, that is

$$\Delta R_{1234}/N\Delta t-\Delta R_{1564}/N\Delta t=\gamma C/N \quad (13)$$

also that at 25 C

$$R_{1234}/N-R_{1564}/N=C/N \quad (14)$$

consequently the difference of the temperature coefficients is equal to the temperature coefficient of the copper times the proportional difference of the resistances.

If the resistance element is in the form of a sheet or number of sheets in parallel with the upper edge on a level with the points of attachment of the potential connections 2 and 3 and the lower edge on a level with the points of attachment of the potential connections 5 and 6, the arrangement would be somewhat similar to that which would be obtained with a large number of similar wires uniformly spaced.

Ordinarily α has a value in the range from -0.00001 to $+0.00003$, β has a value in the range from -0.0000002 to -0.0000006, γ is approximately 0.0038, if the current posts are of copper having the normal conductivity; δ is less than 0.0038; and in many, if not most, cases, $D\delta/nN$ is less than 0.00001. If, therefore, C/N is as large as 0.01, it is very probable that at temperatures in the vicinity of 25 C, the resistance R_{1234} will increase with an increase of the temperature and that the resistance R_{1564} will decrease with an increase of the temperature. If the two sets of potential connections were removed and other potential connections made on the current posts at points between the upper and lower wires or upper and lower edges of the manganin sheet, the resistance would be less than R_{1234} and greater than R_{1564}. Also, the rate of change of the resistance with temperature would be less than that of R_{1234} and greater than that of R_{1564}.

Consequently if C/N is sufficiently large, by a proper selection of the point of attachment of the potential connections a zero rate of change of resistance with temperature at a selected temperature, such as 20 or 25 C, may be realized. Further, a reduction of the section of the current posts between the upper and lower manganin wires or upper and lower edges of the manganin sheet and above the points of attachment of the potential connection decreases the resistance and the rate of increase of the resistance with temperature. Also, a decrease of the section of the current posts between the upper and lower manganin wires or upper and lower edges of the manganin sheet and below the points of attachment of the potential connections increases the resistance and the rate of increase of the resistance with temperature. Finally, any relatively small change in resistance made by changes wholly on the current posts changes the rate of change of resistance with temperature an amount equal to the temperature coefficient of

the copper current posts times the proportional change in the resistance, as may be seen for a special case by a comparison of equations (14) and (13); while obviously any relatively small change in resistance made wholly on the manganin, in such manner as not to perceptibly change the current distribution in the copper, has but little effect on the rate of change of the resistance with temperature.

These conclusions are applicable only in case of a particular type of dissymmetry such as exists in most low-valued precision resistance standards and then only to the extent that the current in the current posts may be considered to be in the direction of their length. They do not apply at all in case of a symmetrical or approximately symmetrical construction, such as is used for some of the heavy-current resistance standards.

III. EXPERIMENTAL RESULTS

The first resistance standard selected for adjustment of its temperature coefficient was a Wolff 0.001 ohm, constructed approximately 30 years ago. The resistance element consists of two manganin sheets in parallel, each having a width of about 5.5 centimeters and a length of about 13 centimeters. Initially, the potential connections were at the level of the center of the manganin sheets and the rate of increase of resistance with the temperature was 22.5 parts per million per °C at 25 C. The intention was to reduce the rate of change of resistance with temperature at 25 C to substantially zero, even though a rough calculation indicated that this would require a greater reduction in the resistance than could be obtained by moving the points of attachment of the potential connections. It was therefore decided to move the potential connections to the bottoms of the current posts, which is equivalent to moving them to points opposite the lower edges of the manganin sheets; redetermine the temperature coefficient, and compare the change with that estimated from the known resistance, dimensions, and assumed values for the conductivity and temperature coefficient of the current posts; then to make further adjustments of the temperature coefficient by reducing the section of the current posts; and finally to readjust the value of resistance without materially changing the temperature coefficient. After having moved the potential connections to the bottoms of the current posts a redetermination of the temperature coefficient showed that it has been reduced substantially the expected amount. However, the resulting change in the resistance was not observed. Then the sections of the current posts were reduced sufficiently to give a total reduction in the resistance equal to that considered necessary to give a zero temperature coefficient at 25 C. Then a redetermination of the temperature coefficient showed that while it had been further reduced it was still far from the desired value.

Further reduction of the sections of the current posts resulted in further reductions of the temperature coefficient, but the discrepancy between the change in resistance and expected change in temperature coefficient was so great as to indicate clearly that some unjustifiable assumption had been made. When the temperature coefficient had been reduced to substantially zero, the reduction of the resistance was found to be approximately 2½ times the estimated amount. In attempting to locate the cause of the discrepancy, it

was suspected that the temperature coefficient of the copper current posts might be abnormally low, as they are of cast copper. As a direct measurement of the temperature coefficient of the current posts would have presented considerable difficulty, their conductivity was measured and found to be only about 40 percent of normal, so that presumably their temperature coefficient is only about 40 percent of normal. At any rate, the assumption of both the 40 percent normal conductivity and the 40 percent normal temperature coefficient brings observed and expected results into accord. The resistance of the standard was then increased to the desired value by enlarging holes in the manganin sheets as was done in the original adjustment. This decreased the ratio of the copper to the manganin resistance by about 1.5 percent without perceptibly changing the current distribution in the copper. Presumably, therefore, it changed the temperature coefficient about -1.5 percent of about -0.00002, the estimated contribution of the copper to the temperature coefficient of the standard, or about $+0.0000003$, an amount too small to be definitely checked experimentally.

Similar experiments were made on other resistance standards in which the current posts are of drawn copper and therefore presumably have normal values of resistivity and temperature coefficient. The resistance element of each of these standards consists of two or more wires in parallel. Changing the locations of the potential connections on the current posts, or reducing the cross section of the current posts when the potential connections were at the bottoms of the current posts, produced changes in the temperature coefficient equal to 0.0038 times the relative change in the 4-terminal resistance of the standards, within the experimental error in measuring the temperature coefficients.

IV. RESISTANCE ADJUSTMENTS

In the construction of resistance standards the ratio of the length to the section of the resistance material cannot be so chosen as to give accurately the desired resistance. Furthermore, after the resistance element has been brazed to the current posts the length cannot conveniently be changed nor the section increased. Therefore, it is customary to make the ratio of the length to the sections such as to give a resistance somewhat low and then bring it up to the desired value by decreasing the section. If, accidentally, the section is reduced too much, or in case the resistance of a standard has increased since its original adjustment, the usual procedure is to attach a shunt of such resistance as will lower the resistance of the standard to the desired value.

As pointed out above, lowering the points of attachment of the potential connections or a reduction of the sections of the current posts below the upper manganin wire or upper edge of the manganin sheet or sheets and above the points of attachment of the potential connections reduces the resistance. This procedure is more convenient and better than the attachment of a shunt.

Should the proposed reduction in the unit of resistance (amounting to about 47 parts in 100,000) be adopted, most of the low-valued precision resistance standards now in use could be made to accord with the new unit by this procedure. Since on the average the resistances

of these standards are high by about 10 parts in 100,000 the average reduction would amount to about 57 parts in 100,000.

As most of these standards have copper current posts, an average reduction of 57 parts in 100,000 in the resistance by changes wholly on the current posts would reduce the temperature coefficient on the average about 2 parts in 1,000,000. While in most cases some reduction of the temperature coefficient would be beneficial, such a small reduction would be scarcely significant.

V. LOAD COEFFICIENTS

The current in a resistance standard causes the resistance element to assume a temperature higher than that of the surrounding medium, by an amount approximately proportional to the I^2R loss in the element, sometimes called the load.

The load coefficient may be defined as the proportional increase in resistance divided by the load. It is generally assumed that, in cases of equal opportunity for the dissipation of the heat, the load coefficients are proportional to the temperature coefficients. While in general this has been found to be true, a considerable number of exceptions have been observed. Usually it has been assumed that these exceptional cases result from strains caused by unequal heating of the resistance element. There is, however, another and possibly more probable reason for many of these exceptions. The temperature rise in the current posts, in general, is small relative to that in the resistance element. Consequently, the load coefficients should be expected to depend mainly on the temperature coefficients of the resistance elements. Therefore, in cases in which the current posts have a material but more or less random effect on the temperature coefficients of resistance standards, it should not be expected that ratios of the load coefficients would be equal to the ratios of the temperature coefficients, even in cases of strictly equal opportunities for the dissipation of heat. Furthermore, a change in the temperature coefficient brought about by changing the location of the potential connections or sections of the current posts should have little or no effect on the load coefficient.

WASHINGTON, October 12, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP640

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

WEAR OF CARPETS

By Herbert F. Schiefer and Richard S. Cleveland

ABSTRACT

The nature of the wear on the wool fibers was studied microscopically. The wool fibers from a worn carpet are frayed at the tips and spindle-shaped fibrils whose dimensions correspond to cortical cells are worn off. Some of the fibers are fractured, others are broken off near the base by the repeated bending and compression. The carpet wear test furnishes a new and easy means of obtaining and isolating the cortical cells of the wool fiber.

A wear index which is applicable to all ordinary kinds and qualities of pile carpets and which is believed to give a good representation of their relative durability in service has been selected and used in this paper.

The effect of the quality of pile wool, height of pile, density of pile, type of pile anchorage, and carpet underlays on the durability was studied. The density of the pile appears to be the predominant factor of a carpet which affects wear. The height of pile is a factor of lesser importance. The quality of pile wool has a measurable effect. The types of pile anchorage studied have no appreciable effect. In general, the wear index is approximately proportional to the product of pile density squared and pile height.

All underlays increased the durability of the carpets. The increase in wear index depends upon the underlay and the carpet. The composition, thickness, density, and compressibility of underlays are factors which contribute to their effectiveness. An underlay appears to be more effective when it is used with carpets of short pile than when it is used with carpets of long pile.

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I. INTRODUCTION

Since the publication of Research Paper No. 315 describing a "Carpet Wear Testing Machine", [1] numerous tests of the wear of carpets have been made at the Bureau of Standards. Attention has been given to the nature of the wear on the wool fibers. The effect on the durability of carpets of quality of pile wool, height of the pile, density of the pile, type of pile anchorage, and the effect of carpet underlays have been studied.[2] The results obtained indicate that

[1] Schiefer, H. F. and Best, A. S., Carpet Wear Testing Machine, B.S. Jour. Research, vol. 6 (RP315) pp. 927-936, June 1931.

[2] By "pile" is meant the face or nap of the carpet. See figure 9. By "underlay" is meant the layer of material which is frequently placed underneath the carpet to reduce slipping on the floor and to increase the softness and durability.

the wear produced by the machine is similar to that produced in service and they indicate a direct correlation between serviceability and the machine wear index.

The results should be of interest to both manufacturer and user of carpets because they suggest, on the one hand, ways to improve carpets to meet the varying requirements of the customers, and on the other, a basis for the selection of carpets with reference to relative durability.

II. TEST PROCEDURE

The testing machine is shown in figure 1. A circular sample of the carpet to be tested is fastened to a turntable which is brought to bear against two leather-covered pulleys. One of the pulleys is driven by a motor and in turn drives the turntable. The other pulley is used as a brake to produce slipping of both pulleys on the carpet as it rotates. A vacuum cleaner removes the material which is worn off. The wear is evaluated by measuring the change in thickness of the pile as the test proceeds.

The tests were made under the following conditions:

Downward force at each pulley	135 lb.
Brake load	15 lb.
Speed of turntable	80 rpm.
Relative humidity	65 percent.
Temperature	70 F.

Thicknesses were measured with the gage shown in figure 2, having a circular foot 1 inch in diameter and exerting a pressure of 0.75 lb/sq in. The total thickness of the carpet was determined before wear and at intervals during the test. The measurements were made at 8 points spaced 45° apart on the circular worn portion of the carpet and the results averaged. The thickness of the backing of the carpet was determined by pulling out the pile tufts from a sufficiently large area to permit measurements in several places. The thickness of the pile was then obtained by subtracting the thickness of the backing from the thickness of the carpet. When a carpet was tested with an underlay, the carpet was removed from the testing turntable to another turntable for thickness measurements. The thickness of the underlay was measured while the underlay was still in its undisturbed position on the testing turntable.

A test was discontinued when the pile had been worn down to one fourth of the original pile thickness. Discontinuing the tests at this point protected the leather from rapid deterioration by contact with the coarse backing and kept the surface smooth. Under these conditions the pulleys had to be refaced with new leather at intervals of approximately 1,500,000 revolutions of the turntable.

III. RESULTS

1. WEAR INDEX

The number of thousands of revolutions of the turntable required to wear the pile of a carpet down to one fourth of the original pile thickness was taken as the wear index of the carpet. This index was selected after consideration of other methods of evaluating wear. It has the advantage of being applicable to all ordinary kinds and qualities of pile carpets. The wear indices correlate well with the

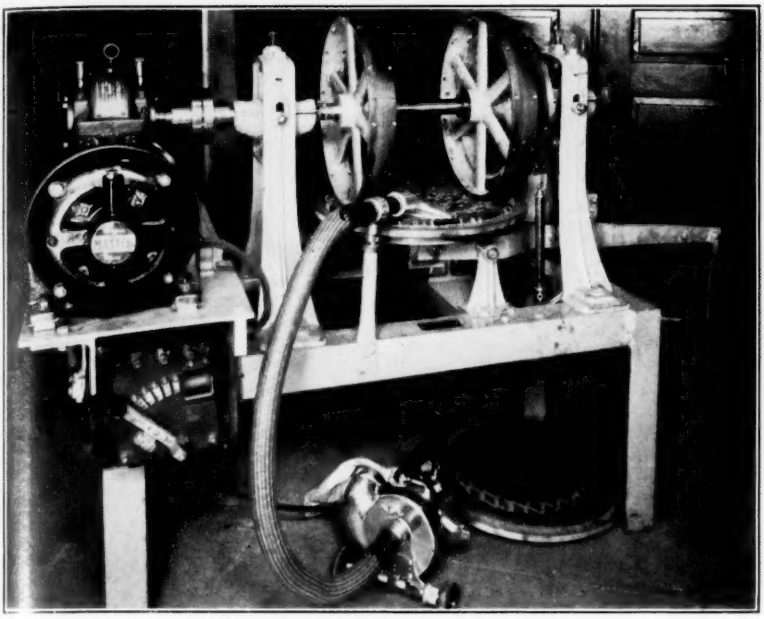

FIGURE 1.—*Carpet wear-testing machine.*

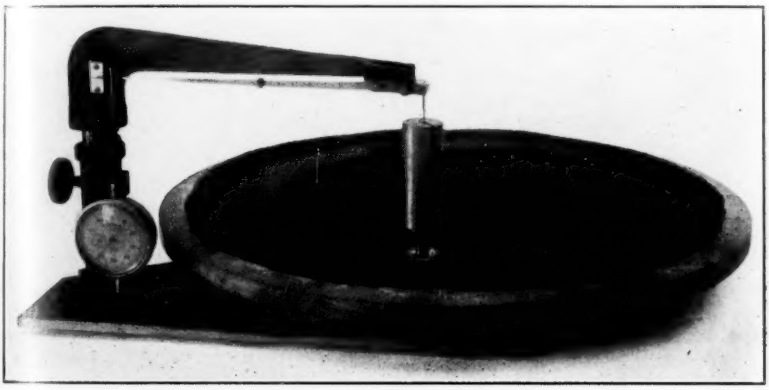

FIGURE 2.—*Gage for measuring thickness of carpet.*

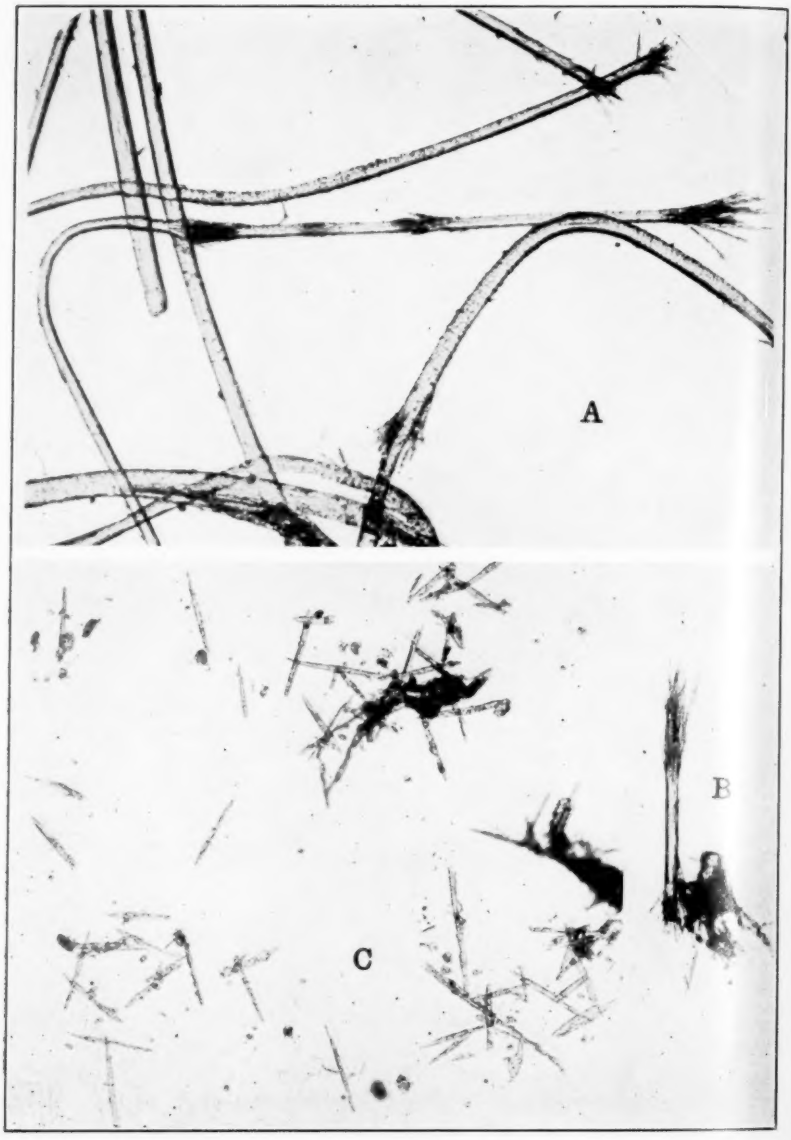

FIGURE 4.—*Nature of accelerated wear on wool fibers.*

A, Wool fibers removed from worn track of carpet. Fibers show characteristic fraying and partial fractures. Magnification about 50.

B, Segment of fractured wool fiber removed from worn track of carpet by vacuum. Segment shows characteristic fraying at both ends. Magnification about 50.

C, Fibrils removed from worn track of carpet by vacuum cleaner. They have the characteristic spindle-shaped appearance of cortical cells of wool fibers and correspond to them in dimensions. Magnification about 200.

available manufacturer's wear indices, which are based upon the reputation of the carpets in service. In figure 3 are plotted the laboratory wear indices of 4 axminster carpets against the manufacturer's wear indices. The linear relationship between the two indices indicates that the laboratory wear index gives a good representation of the relative durability of these carpets in service.

2. WEAR ON FIBERS

The nature of the accelerated wear on the individual fibers is shown in figure 4. Microscopic examination of fibers taken from carpets after several years in service show similar wear. The tips of the fibers are frayed and split. Some of the fibers are fractured in one or more places. The fibrils at the tips and segments of the fibers are broken off during a test.

The splitting off of the fibrils at the tips constitutes a slow process of wear and is probably produced mainly by the slipping action of the machine. The breaking off of the fibers near the anchorage constitutes a rapid process of wear and is probably produced mainly by the bending and compressive actions of the machine. The slight twisting action of the machine contributes to both wearing processes.

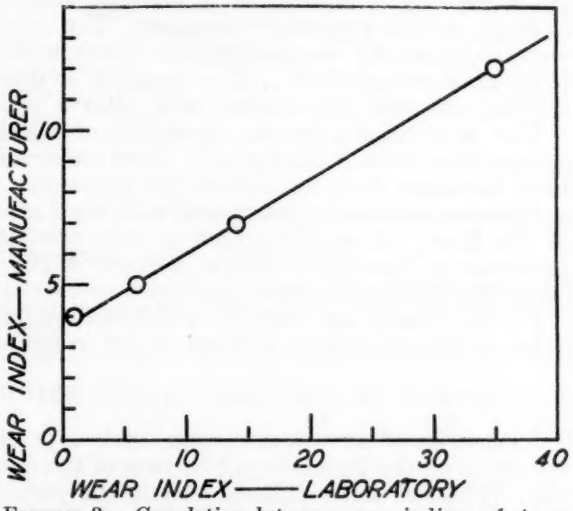

FIGURE 3.—*Correlation between wear indices of 4 axminster carpets based upon laboratory tests and the reputation of the carpets in service.*

The characteristic spindle-shaped appearance of the fibrils shown in figure 4 (*C*) indicates the cellular structure of the wool fiber. The fibrils are arranged with their long axes parallel to the length of the fiber as shown by *A* and *B* of figure 4. The length and maximum thickness of 30 fibrils were measured. The lengths varied from 25 to 58 microns and the maximum thicknesses from 2.5 to 5.0 microns. According to Matthews [3] the lengths of the spindle-shaped cortical cells of wool vary from 36 to 64 microns and the thicknesses from 13 to 17 microns. The dimensions given by Matthews are based upon measurements of cells which were isolated by swelling the wool fiber in an alkali. The swelling takes place mainly in the thickness and little in the length. The amount of swelling of the cells is not known. A determination of it presupposes known values for the dimensions of the cells. It is not surprising therefore, that the thicknesses reported by Matthews are 3 to 5 times those shown in figure 4 (*C*). The close

[3] Textile Fibers, 4th edition, p. 93, 1924.

correspondence in appearance and dimensions identifies the fibrils in figure 4 (*C*) with the cortical cells of the wool.

The carpet wear test furnishes a new and easy means of obtaining and isolating the cortical cells of the wool fiber. This makes it possible to study the behavior of the cortical cells under various conditions. It would be interesting, for example, to determine whether or not the cortical cells aline themselves in a definite fashion when they are suspended in solutions of different pH to which are applied electric or magnetic fields. The method used by Harris [4] in observing the mobility of particles of the wool fiber in the electrophoresis cell could probably be used for such a study.

Gabriel [5] has examined cortical cells of different kinds of wool. He found that the cortical cells of extremely fine Australian Merino fibers were remarkably similar to those of the coarse Lincoln fibers. He noted slight differences in average length, variation from the average, and in general appearance. The cortical cells for his study were obtained by inoculating the fibers with a bacterium isolated from pink rotted wool. The resulting action causes the fibers to disintegrate into free cortical cells after a period of about 10 days.

The wool fiber is known to consist of micelles which are long in comparision to their thickness.[6] They are probably lamellar in shape, their thickness does not exceed 200 angstroms or two millionths of a centimeter, and they are arranged with their axes parallel to the length of the fiber. It is of interest to note that the average maximum thickness of the fibrils shown in figure 4 (*C*) is approximately 160 times the thickness of the micelles.

E. M. Scheid has recently published photographs of worn wool fibers of carpets similar to those shown in figure 4 (*A*).[7]

3. EFFECT OF THE DENSITY AND HEIGHT OF THE PILE [8]

Two series of 12 velvet carpets each were obtained for a study of the effect on the durability of carpets of the density and height of the pile. The two series differed only in the yarn used in the pile. The yarn of series A was stock dyed and the average weight was 0.3 grain per inch length. The yarn of series B was skein dyed and the average weight was 0.28 grain per inch length. The carpets in each series were made in 3 different pile densities by using 3 pitches, namely, 7, 8, and 8.75. Pitch refers to the number of pile tufts per inch of width. The carpets in each series were made in 4 different pile heights for each pitch by varying the height of the wires over which the pile loops are formed before they are cut by withdrawal of the wires. The heights of the wires were 0.114, 0.205, 0.290, and 0.500 inch. The rows, that is, the number of pile loops or wires per inch of length, were kept constant for the two series, namely, at 9 rows per inch.

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[4] The Isoelectric Point of Wool, Milton Harris, B.S. Jour. Research, vol. 8, pp. 779–786, 1932.

[5] The Cortical Cells of Merino, Romeny and Lincoln Wools, M. T. Gabriel, Jour. Textile Institute, vol. 23, no. 8, pp. T171–T176, August 1932.

[6] The Constitution of the Keratin Molecule, Speakman and Hirst, Transaction of the Faraday Society vol. 29, part I, pp. 148–164, January 1933.

[7] Ein neues Schnellverfahren zur Prüfung der Haltbarkeit von Teppichen, E. M. Scheid, Melliand Textilberichte, Band 14, Lieferung 6, Seite 287, Juni 1933.

[8] "Pile height" is the length of the pile tuft projecting above the back. It is measured with a steel scale. "Pile thickness" is the thickness of the pile obtained according to the procedure described under part II. Since the measurements are made under a pressure of 0.75 lb/sq in., pile thickness is less than the pile height. It is used in the evaluation of the durability of the carpet. "Wire height" is a term used by the manufacturer to denote the size of the wire over which the pile loops are formed and is approximately equal to the pile height.

In figure 5 are plotted curves for the series of carpets made from pile yarn A. The thicknesses of the pile are plotted as ordinates

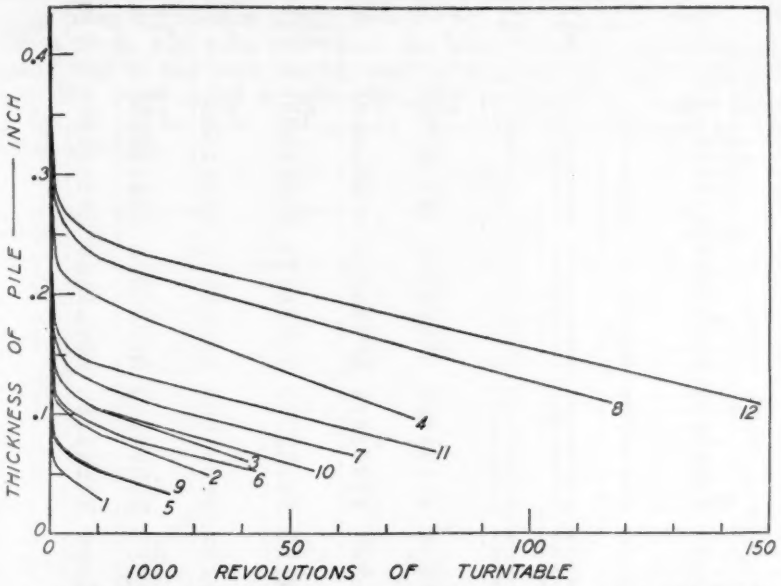

FIGURE 5.—*Curves showing the change in pile thickness with the number of revolutions of the turntable for velvet carpets made from pile yarn A. The numbers are the carpet numbers given in table 1.*

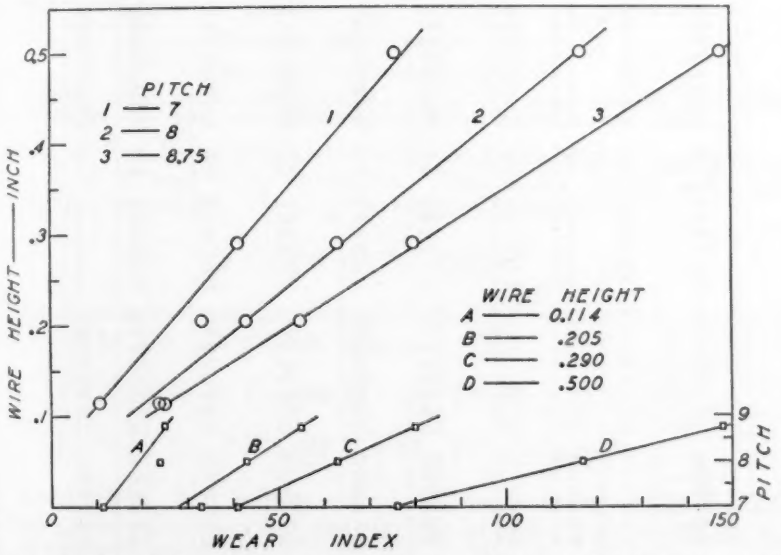

FIGURE 6.—*Correlations of wear index with wire height and pitch for series of velvet carpets made from pile yarn* A.

and the revolutions of the turntable as abscissas. The curves are typical of all of the carpets tested. They show the rate of wear of the pile as judged by change in thickness of the pile.

TABLE 1.—*Analysis of carpets and test results*

No.	Weave	Pile yarn	Rows per inch R	Pitch per inch P	Weight per tuft w	Length of tuft l	Weight of tuft per inch length	Height of pile [1] h	Thickness of pile [2] t	Wear index I	$\frac{(\text{Density})^2(\text{Pile height})}{4R^2P^2w^{\frac{1}{2}}-\frac{1}{2}h}$
					Grains	*Inches*	*Grains*	*Inch*	*Inch*		
1	Velvet	A	9.3	6.7	0.112	0.38	0.295	0.13	0.115	11	175
2	do	A	9.3	6.7	.173	.56	.309	.23	.194	33	341
3	do	A	9.3	6.7	.211	.69	.306	.27	.238	41	392
4	do	A	9.3	6.7	.329	1.10	.299	.48	.389	76	667
5	do	A	9.3	7.8	.113	.37	.305	.14	.140	24	275
6	do	A	9.3	7.8	.164	.54	.303	.23	.209	43	447
7	do	A	9.3	7.8	.205	.69	.297	.27	.258	63	502
8	do	A	9.3	7.8	.314	1.11	.283	.50	.432	117	844
9	do	A	9.3	8.4	.112	.38	.295	.14	.137	25	297
10	do	A	9.3	8.4	.168	.57	.295	.22	.213	55	468
11	do	A	9.3	8.4	.205	.70	.293	.28	.276	80	588
12	do	A	9.3	8.4	.320	1.10	.291	.49	.436	148	1014
13	do	B	9.3	6.7	.112	.40	.280	.14	.128	9	170
14	do	B	9.3	6.7	.163	.58	.281	.22	.174	18	270
15	do	B	9.3	6.7	.204	.71	.287	.25	.232	30	321
16	do	B	9.3	6.7	.317	1.09	.291	.47	.387	55	617
17	do	B	9.3	7.8	.106	.39	.272	.13	.126	12	202
18	do	B	9.3	7.8	.152	.56	.271	.22	.187	38	341
19	do	B	9.3	7.8	.189	.69	.274	.27	.246	59	427
20	do	B	9.3	7.8	.306	1.06	.289	.44	.385	109	772
21	do	B	9.3	8.4	.109	.41	.266	.15	.136	19	260
22	do	B	9.3	8.4	.168	.56	.300	.22	.207	44	484
23	do	B	9.3	8.4	.194	.72	.269	.28	.274	68	498
24	do	B	9.3	8.4	.319	1.08	.295	.46	.410	134	960
25	do	C	8.8	7.9	.103	.37	.278	.14	.127	15	210
26	do	C	8.8	7.9	.155	.55	.282	.22	.212	44	338
27	do	C	8.8	7.9	.200	.66	.303	.28	.272	73	498
28	do	C	8.8	7.9	.243	.82	.296	.36	.342	129	613
29	do	C	8.8	7.9	.301	1.09	.276	.48	.451	178	707
30	do	D	10.0	8.0	.101	.47	.215	.18	.166	21	213
31	do	E	9.0	9.5	.080	.37	.216	.14	.137	22	192
32	do	F	9.9	8.0	.110	.53	.207	.19	.157	25	215
33	do	G	9.0	9.5	.101	.50	.202	.19	.174	29	227
34	do	H	8.8	9.6	.081	.39	.207	.16	.133	29	198
35	do	I	9.0	8.0	.141	.47	.300	.19	.176	34	354
36	do	J	9.0	9.4	.087	.31	.281	.14	.135	35	316
37	do	K	9.2	7.8	.134	.47	.285	.17	.152	37	284
38	do	L	9.0	9.5	.142	.69	.205	.28	.276	59	347
39	do	M	8.8	7.1	.195	.65	.300	.27	.240	73	381
40	do	N	8.8	7.9	.203	.66	.308	.28	.275	85	513
41	do	O	9.0	8.0	.201	.65	.309	.27	.267	89	534
42	Axminster.	P	6.7	7.0	.138	.66	.209	.22	.124	1.7	85
43	do	Q	6.7	7.0	.124	.69	.180	.23	.143	2.4	65
44	do	R	6.7	7.0	.129	.66	.195	.20	.157	2.9	67
45	do	S	6.7	7.0	.133	.69	.193	.24	.123	4.9	79
46	do	T	5.8	7.0	.136	.72	.189	.25	.140	3	59
47	do	U	5.5	7.0	.174	.78	.223	.30	.173	6	89
48	do	V	7.3	7.0	.144	.78	.185	.25	.183	8	88
49	do	W	7.3	6.9	.182	.84	.217	.31	.190	14	148
50	do	X	5.7	7.0	.262	.87	.301	.28	.200	16	161
51	do	Y	5.7	7.0	.233	.75	.311	.28	.200	16	172
52	do	Z	9.6	7.0	.147	.75	.196	.28	.201	23	194
53	do	a	7.0	7.0	.280	.94	.298	.32	.244	26	273
54	do	b	7.1	7.0	.253	.75	.337	.28	.250	30	315
55	do	c	11.8	7.0	.120	.54	.222	.19	.175	35	266
56	Wilton	d	8.8	8.8	.071	.48	.148	.19	.146	11	100
57	do	e	8.9	9.2	.051	.41	.124	.19	.155	14	93
58	do	f	8.9	9.3	.078	.34	.229	.14	.131	16	203
59	do	g	10.3	9.4	.094	.50	.188	.19	.142	31	252
60	do	h	13.4	9.4	.093	.45	.207	.19	.151	34	515
61	do	i	8.9	9.5	.204	.91	.224	.34	.289	35	488
62	do	j	13.2	9.4	.082	.49	.167	.19	.173	55	327

[1] Height of pile is measured with a steel scale.
[2] Thickness of pile is measured with a gage having a circular foot 1 inch in diameter and exerting a pressure of 0.75 lb/sq in.

The analyses and wear indices of the two series of carpets are given in table 1, numbers 1 to 24, inclusive. Judged by wear indices, series A is slightly superior to series B. This is mainly due to the heavier pile yarn used in series A.

For a given pile yarn and pitch the wear index is approximately proportional to the wire height, and for a given pile yarn and wire height the wear index is approximately proportional to the pitch (see fig. 6). The wear index may therefore be expressed by the general equation

$$I=(a\ P+b)\ (c\ W+d)+e$$

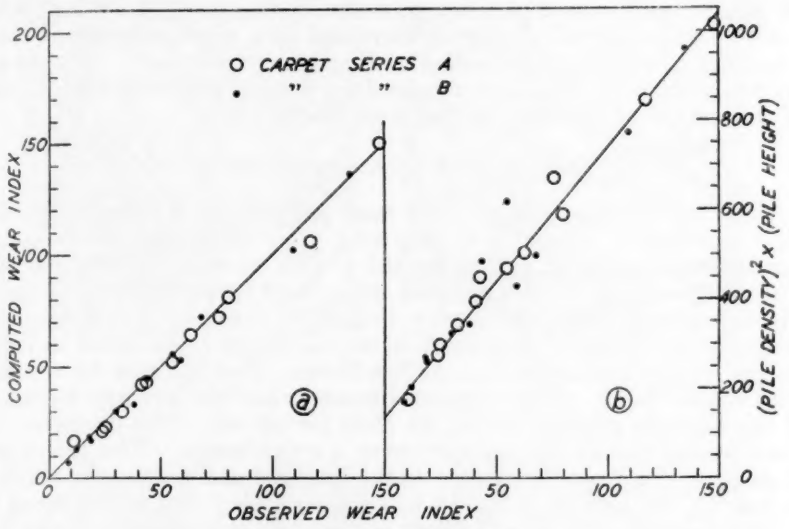

FIGURE 7.—*Correlation curves.*

(*a*) Correlation between observed and computed wear indices; (*b*) Correlation between observed wear index and product of pile density squared and pile height, for the two series of velvet carpets.

where I, P, and W are wear index, pitch, and wire height, respectively, and a, b, c, d, and e are constants. This is the equation for the hyperbolic paraboloid. It may be reduced to the form

$$I=a'PW+b'P+c'W+d'$$

and the constants determined empirically. The data are represented fairly close by the following equations:

$$I=106\ PW-9\ P-600\ W+64 \quad \text{for pile yarn A, and}$$

$$I=107\ PW-7\ P-625\ W+42 \quad \text{for pile yarn B.}$$

For comparison, the indices computed from these equations are plotted against the observed wear indices in figure 7(*a*) which shows a good linear relationship.

It is to be noted that the wear index increases more rapidly with increase in pitch (density) than with increase in pile height (wire

height). There is a fairly good correlation between the wear index and the product of pile density squared and pile height. This product is equal to $4\ R^2\ P^2\ w^2\ l^{-2}h$, where R is rows per inch, P is pitch per inch, w is weight per tuft in grains, l is length of tuft in inches, and h is height of pile in inches. The products are given in the last column of table 1. They are plotted against wear indices in figure 7(*b*) which shows a fairly good linear relationship.

The important conclusion to be drawn from these tests is that the density of the pile is the predominant factor which affects the rate of wear of the pile. The height of the pile is a factor of lesser importance. In other words, the durability of a carpet is increased by a greater amount when the pile density is increased by a given percentage than when the pile height is increased by the same percentage. The difference in durability may be accounted for readily from a consideration of the nature of the wear on the wool fibers.

4. EFFECT OF THE QUALITY OF PILE WOOL

The effect of the quality of pile wool is shown by the results for the four axminsters, nos. 42, 43, 44, and 45. These four carpets are similar to one another except for the quality of wool used in the pile. The analyses and wear indices of these carpets are given in table 1. Photographs of the wool fibers are shown in figure 8. It is to be noted that the diameters of the fibers in no. 42 range from small to large values with a preponderance of fine fibers. Nos. 43 and 44 contain very coarse fibers. The range of diameters and the average diameter of the fibers is greater for no. 43 than for no. 44. The diameters of the fibers of no. 45 do not vary over a great range. The fibers are of medium diameters compared to the fine and coarse fibers contained in nos. 42, 43, and 44. No. 45 has a wear index of 4.9 compared to 1.7 for no. 42. The wear indices for nos. 43 and 44 are 2.4 and 2.9 respectively.

The pile consisting of fine fibers is readily compressed and many of the weak fibers are probably broken off during the early part of the test by the slipping and twisting actions of the machine. This undoubtedly accounts for the low wear index of no. 42. The pile consisting of very coarse fibers is not readily compressed. The coarse, stiff fibers are probably readily fractured near the anchorage by the repeated bending action of the machine. This may account for the low wear indices of nos. 43 and 44. The fibers of medium diameters on the other hand are strong enough to better withstand the slipping and twisting actions and are flexible enough to better resist fracturing due to the bending actions. This accounts for the high wear index of no. 45. The quality of the wool used in the pile appears to have a direct influence on the nature and rate of wear of the wool fibers.

Ashcroft has published results showing the rate of wear of the pile as it is affected by the boiling of the yarn in the dyeing process.[9] His results indicate that the rate of wear increases almost directly with the time of boiling. This probably accounts for the uneven wear which the authors observed in carpets in which the pattern consisted of several colors. Yarns of certain colors were observed to wear more rapidly than adjacent yarns of other colors.

[9] Melliand Textile Monthly, vol. 4, no. 12, pp. 721–724, March 1933.

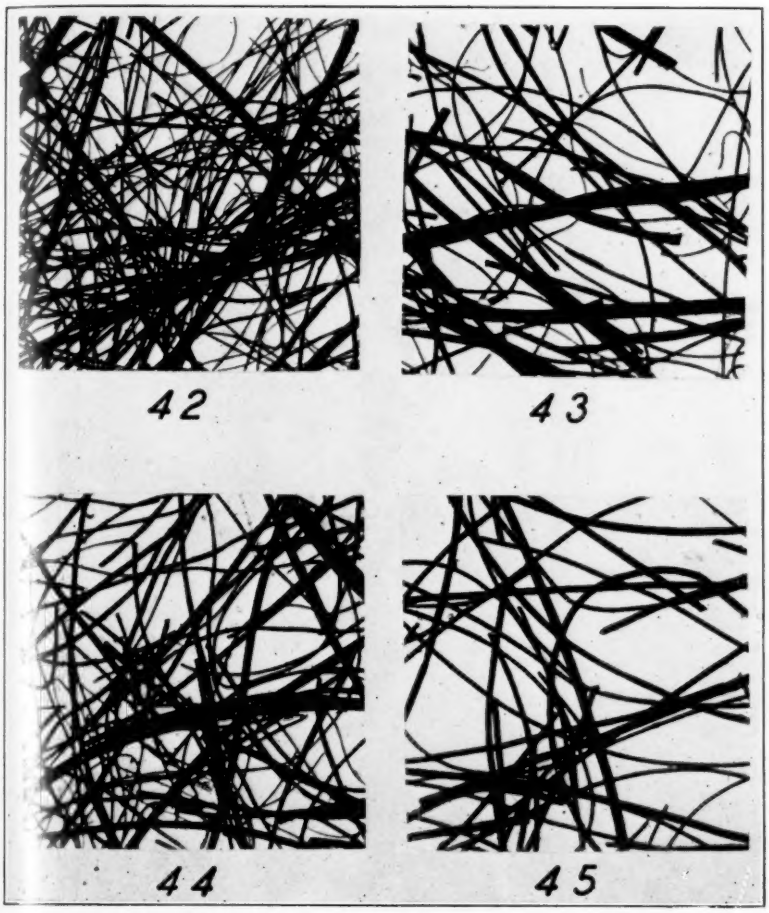

FIGURE 8.—*Photographs of wool fibers showing variations in diameter.*
The numbers indicate the carpets in table 1 in which the wool is used as pile.

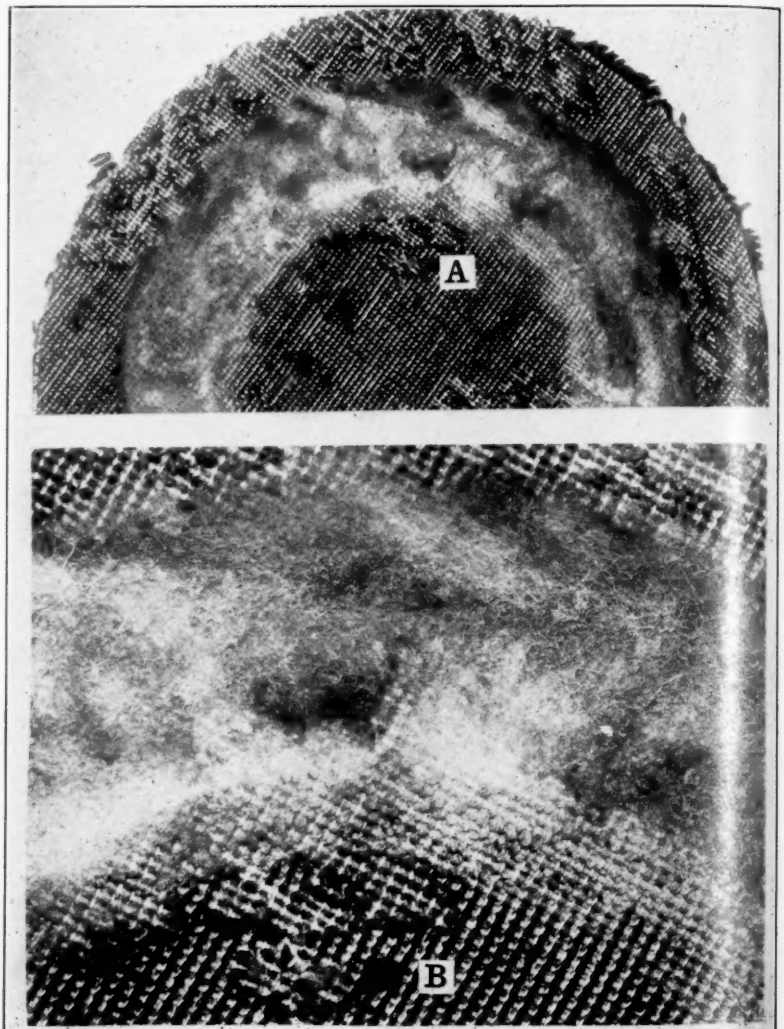

FIGURE 10.—*The back of a carpet, which had its pile through-to-the-back, after a test.*
B is a portion of A magnified 2.6 times.

These results suggest the importance of the fiber blend and the quality of the pile wool and indicate a fruitful field for further study.

5. EFFECT OF THE TYPE OF PILE ANCHORAGE

It is difficult to determine the effect of the pile anchorage on the durability. Carpets usually differ greatly in other factors, such as pitch, rows, pile heights, and yarn size, which have a greater effect on the durability and which mask the effect of the type of pile anchorage.

Typical pile anchorage are shown in figure 9. Tests made on a five-frame wilton carpet and on a velvet carpet, which were specially woven alike in all respects except anchorage of pile, showed no difference in the rate of wear.

It is worth while to note the effect of the wear test on a carpet having the pile tufts exposed on the back. When this carpet was

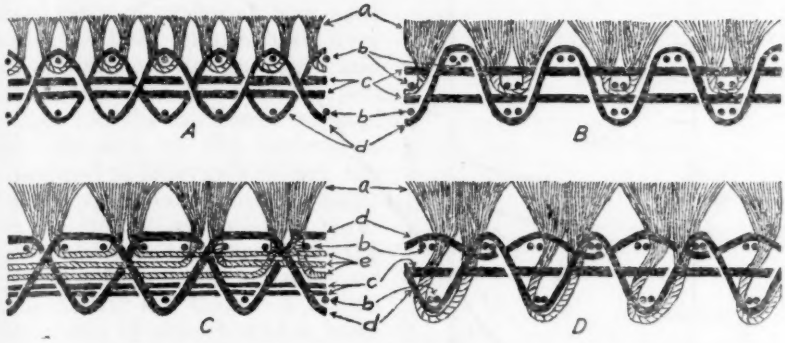

FIGURE 9.—*Diagrammatic cross sections of carpets.*

Type:
- *A.* Velvet, double-chain, two-shot with two stuffers.
- *B.* Axminster, single-chain, three double shots with two stuffers.
- *C.* Wilton, double-chain, three-shot, three-frame with two stuffers.
- *D.* Axminster, pile-through-to-the-back, double-chain, three double shots with one stuffer.

Parts:
- *a.* Pile, the face or nap of the carpet.
- *b.* Weft or woof, the threads that run crosswise of the carpet. (Shots, the number of times the weft thread is shot across to bind each row of pile.)
- *c.* Stuffers or fillers, extra threads laid lengthwise and crosswise of a carpet to increase bulk, weight, and stiffness.
- *d.* Chain, the longitudinal threads that bind the weft into the body of the carpet. These constitute a part of the warp threads which are the threads that run lengthwise of the carpet.
- *e.* Frames, the number of pile threads in a cross-section of a Wilton or Brussel carpet.

tested, the wool fibers gradually worked through to the back where they became matted together. This condition produced very irregular wear on the pile. The appearance of the back after a test is shown in figure 10. Ashcroft has called attention to a similar effect both in laboratory and service tests.[10]

In addition to the data on the velvet and axminster carpets referred to under sections 3 and 4, there are also given in table 1 similar data on wilton and several other axminster and velvet carpets. The general conclusion that the wear index is approximately proportional to the product of pile density squared and pile height is valid for all the carpets tested. In other words a given percentage increase in density of the pile produces a greater increase in the durability than the same percentage increase in height of pile. The results are shown in figure 11 for all tests on the three weaves. No specific conclusions can be drawn with reference to a particular weave. There is con-

[10] See footnote 9.

siderably more scattering than was the case with the velvet carpets discussed under section 3, figure 7 (*b*). This greater scattering is undoubtedly due to variables which were controlled in the special series of velvet carpets.

6. EFFECT OF UNDERLAYS

To show the effect of carpet underlays on the durability, a number of carpets were tested in combination with underlays. The underlays included: (*a*) three of jute; (*b*) two of animal hair and jute; (*c*) one of

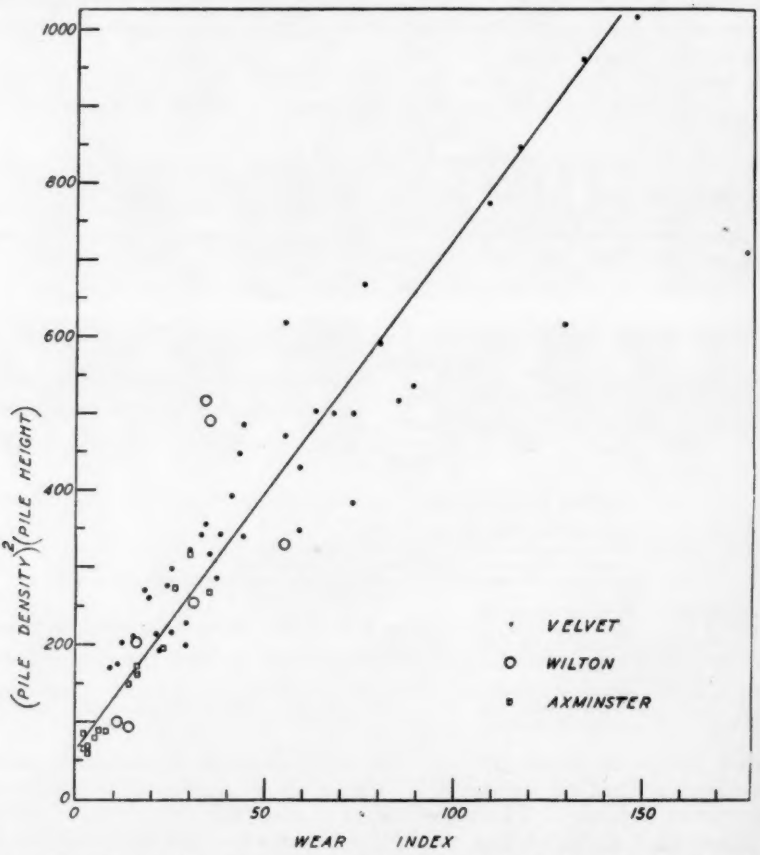

FIGURE 11.—*Correlation of wear index with product of pile density squared and pile height.*

cotton and paper; and (*d*) two of rubber. The carpets which were tested with underlays included velvets, axminsters, wiltons, and a domestic oriental having a long pile. The results are given in table 2.

In group I, specimens of one carpet were tested with the eight different underlays. All underlays increased the wear index of the carpet. The increases varied between 73 and 146 percent. It is to be noted that for the jute underlays, which were greatly compressed during the tests, the wear index is increased when the thickness of the underlay is increased from 0.29 to 0.37 inch, and that it is slightly

decreased when the thickness is further increased to 0.47 inch. This is in substantial agreement with service tests conducted by A. C. Nielson Engineering Co. in the lobby of one of Chicago's largest theaters.[11]

In group II, specimens of seven different carpets were tested with specimens of one underlay. The wear index of each carpet was increased. The increase varied from 7 percent for the domestic oriental with a long pile to 146 percent for the velvet with a short pile. It appears that the underlay is more effective when it is used with carpets of short pile than when it is used with carpets of long pile.

In group III a specimen of carpet was tested with a sponge-rubber underlay, and then the test was repeated on another specimen of the carpet but the same piece of underlay was used underneath it. Similar tests were made with a jute underlay and specimens from the same carpet. In figure 12 the thickness values of the pile and of the underlays, measured at intervals during the tests, are plotted against the number of revolutions of the turntable. The thickness of the sponge-rubber underlay changed little during the tests. The two specimens of carpet which were tested with the same specimen of sponge-rubber underlay had the same increase in wear index, namely, 67 percent. The thickness of the jute underlay decreased greatly during the first test, but the further decrease in thickness during the second test was small. This difference in inelastic compression had a marked effect on the rate of wear. The wear index of the first specimen of carpet tested with the specimen of jute underlay was increased 67 percent, while the wear index of the second specimen tested with the same specimen of jute underlay was increased only 29 percent. These tests indicate that an underlay which is permanently compressed during use becomes less effective. Since rubber is likely to become hard and brittle with age, it is quite possible that the effectiveness of the rubber underlay may also be materially lessened with age.

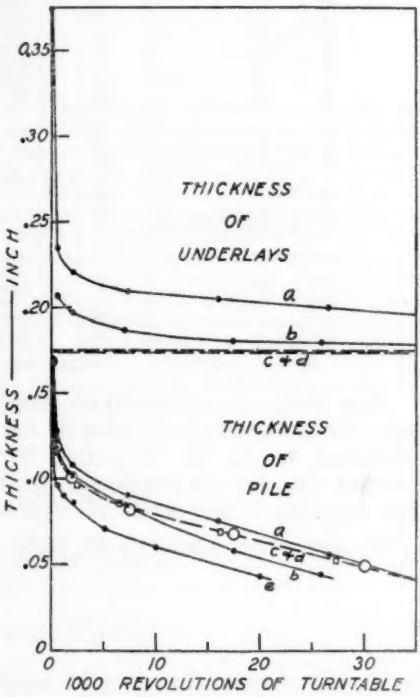

FIGURE 12.—*Curves showing changes in thickness of pile and underlay when two specimens of the same carpet are tested with one specimen of an underlay.*

(*a*) Carpet no. 30 tested with jute underlay B, first test.
(*b*) Same as (*a*) for second test.
(*c*) Carpet no. 30 tested with sponge-rubber underlay B, first test.
(*d*) Same as (*c*) for second test.
(*e*) Carpet no. 30 tested without an underlay.

[11] Letter from Western Felt Works dated May 15, 1931.

TABLE 2.—*Results of tests on carpets and underlays*

Group	Carpet			Underlay				Wear index		
	No.	Weave	Height of pile	No.	Description	Thickness		Carpet	Carpet and underlay	Increase
						Before test	After test			
			Inch			*Inch*	*Inch*			*Percent*
I	63	Velvet	0.15	1	Jute A	0.29	0.15	11	19	73
	63	do	.15	2	Jute B	.37	.19	11	26	136
	63	do	.15	3	Jute C	.47	.27	11	24	118
	63	do	.15	4	Jute and hair	.42	.24	11	26	136
	63	do	.15	5	Hair and jute	.30	.20	11	21	91
	63	do	.15	6	Cotton and paper	.24	.14	11	19	73
	63	do	.15	7	Sponge rubber A	.31	.24	11	19	73
	63	do	.15	8	Sponge rubber B	.23	.23	11	27	146
II	63	do	.15	8	do	.23	.23	11	27	146
	30	do	.18	8	do	.17	.17	21	35	67
	35	do	.19	8	do	.23	.23	34	56	65
	55	Axminster	.19	8	do	.18	.18	35	57	63
	65	Wilton	.30	8	do	.22	.22	22	31	41
	47	Axminster	.30	8	do	.21	.21	6	8	33
	64	Domestic oriental	.55	8	do	.19	.19	56	60	7
III	30	Velvet	.18	8	Sponge rubber B, 1st test.	.17	.17	21	35	67
	30	do	.18	8	Sponge rubber B, 2d test.	.17	.17	21	35	67
	30	do	.18	2	Jute B, 1st test	.39	.20	21	35	67
	30	do	.18	2	Jute B, 2d test	.21	.18	21	27	29

The authors express their appreciation to the 17 manufacturers who have supplied samples of carpets and underlays. We are also indebted to G. E. Hopkins, technical director, Bigelow Sanford Carpet Co., for his personal interest in the tests and in arranging for the weaving of the series of carpets of special constructions.

WASHINGTON, October 30, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP641

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

A GAMMA-RAY IONIZATION CHAMBER FOR USE WITH A DIRECT CURRENT AMPLIFIER

By L. F. Curtiss

ABSTRACT

A description is given of a new type of gamma-ray ionization chamber in which the source is within the central electrode. The chamber is so designed with guard rings that only an annular zone of ionization about the source of gamma rays contributes to the measured ionization current. This arrangment yields ionization currents for average preparations of radium of the order of 10^{-11} amperes. These currents are readily amplified by a vacuum-tube amplifier so as to be readable on a microammeter. This arrangement has been tested in the Radium Laboratory at the Bureau of Standards and found to give results accurately comparable with the determinations made by means of a gold-leaf electroscope. It possesses the advantages over the electroscope that it is more rugged, more easily read, no blank drift need be taken, and the operator may be at a distance from the gamma-ray source during readings. In addition, the source is entirely screened by lead when in position for measurement, and sources of all strengths are measured in the same position. The arrangement is particularly suited to the routine standardization of commercial preparations of radium and radon.

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I. INTRODUCTION

In making gamma-ray comparisons of preparations of radium or radon it is desirable to reduce as far as possible the exposure of the observer to the radiation. This is of greatest importance where large quantities of radium are to be handled. It requires that observations be made as quickly as possible and that the radium should be at a considerable distance from the observer at all times. Many of the devices in general use are far from satisfactory in these respects. As is well known, the inverse square law is the most important factor in reducing exposure to gamma radiation. In devising any new method of measurement, therefore, first consideration should be given to increasing the distance between the preparation and the observer when taking readings. In the case of the gold-leaf electroscope this can only be accomplished by optical means.[1] Consequently the distance at which the observer can conveniently observe the motion of the gold leaf is limited. Furthermore, exposure to radiation cannot be reduced by screening with this method of measurement.

[1] Curtiss, L. F., Jour. Opt. Soc. Amer. and Rev. Sci. Insts., vol. 16, p. 363, 1928.

This paper describes a new type of ionization chamber which, when used with a simple direct-current vacuum-tube amplifier, provides a means of comparing radium preparations and other gamma-ray sources. This method provides greater protection for the operator and reduces the time and labor required for making accurate comparisons.

II. GEOMETRICAL ARRANGEMENT OF THE IONIZATION CHAMBER

When replacing the gold-leaf electroscope by an ionization chamber for use with a vacuum-tube circuit, a considerable simplification of the problem is achieved if a form of chamber is used which yields as large an ionization current as possible for a given preparation. The usual electroscope or ionization chamber utilizes only a small fraction of the total ionization. The maximum current would be obtained by placing the gamma-ray source inside a small spherical electrode at the center of a large hollow sphere. An approximation to this arrangement can be obtained by placing the source in a cylindrical electrode, located on the axis of a cylindrical ionization chamber. This form is easy to construct and yields an ionization current sufficiently larger to be readily amplified and measured.

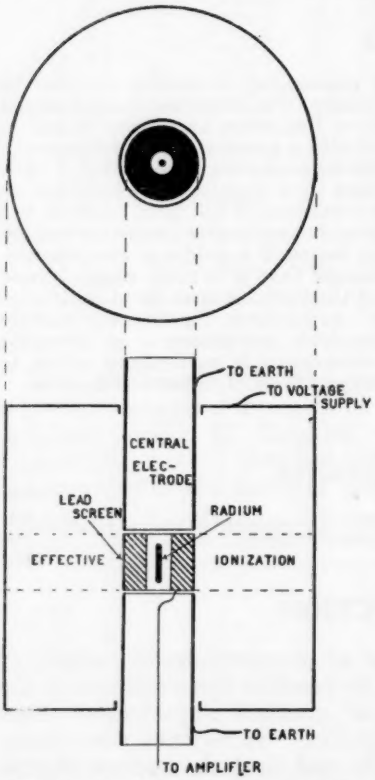

FIGURE 1.—*Diagram of new type of ionization chamber.*

In designing such a chamber precautions must be taken to avoid an arrangement which will cause the corrections for absorption of radiation in the walls of metal containers to vary erratically. The ideal condition would result in these corrections becoming indentical with those determined by use of a gold-leaf electroscope when the preparation is at some distance from the electroscope. It requires that all radiation which does not proceed nearly normal to the axis of the radium needle or tube should be prevented from contributing to the ionization current which is measured. It was found that this requirement is sufficiently satisfied if the ionization included in an annular space (about the preparation) of a height approximately equal to the length of the preparation and an external diameter at least 10 times this length is allowed to contribute to the measured current. The selected arrangement is indicated in the diagram in figure 1. The central cylindrical electrode is composed of 3 sections, the intermediate of which is electrically insulated and provided with a lead connecting it with a device for measuring the current flowing to it.

This insulated section, in the center of which the radium preparation is placed, has thick lead walls to provide proper filtering of the gamma radiation. The upper and lower sections are connected to earth; consequently the ionization current collected by them does not contribute to the measured current. Since the intermediate section never rises more than 1 or 2 hundredths of a volt above earth potential and the difference of potential between the central electrode and outer walls of the chamber is several hundred volts, the electro-static field is practically radial and uniform over the surface of the intermediate section; consequently, the volume of effective ionization is approximately that indicated.

A scale drawing of the vertical section of a chamber constructed according to this design is shown in figure 2. The horizontal sections of all parts are circular. The central electrode made up of three parts, E, C, and D, is assembled into a single rigid unit by means of hard-rubber bushings pressed into the brass sheath of the upper and lower section. The intermediate, insulated section, C, has lead walls 1 centimeter thick. The radium preparation, R, is introduced through the opening at A and held in position on the axis of the electrode by an aluminum holder, not shown. To make possible a fairly deep well in the lead-walled section and thus provide for better shielding of the upper parts of the chamber from softer radiation, this section is made about twice as long as the average radium preparation; but the effective length of the section is limited by the tubular-brass screen, S, attached to the upper section. The annular zone, I, then becomes the volume of effective ionization. Connection to the current-measuring device is made by means of the lead, L, brought out through the center of the hard-rubber bushing in the lower section of the central electrode. The brass outer walls of the ionization chamber are supported by the hard-rubber collars, BB.

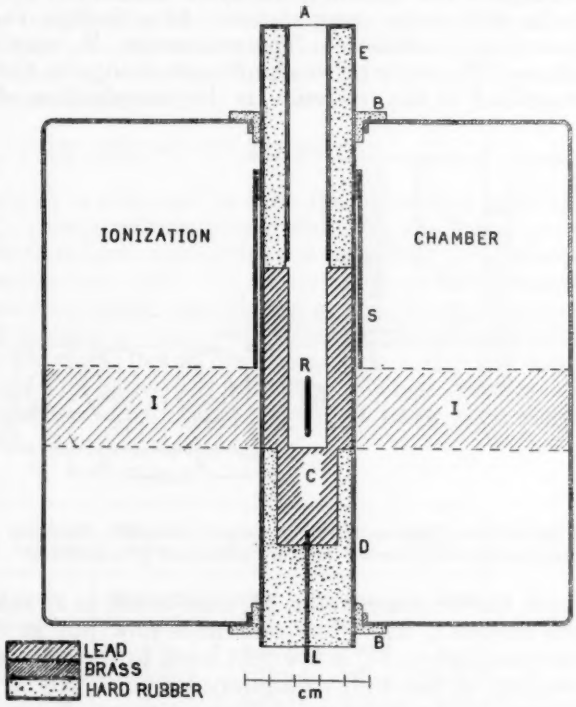

FIGURE 2.—*Vertical cross section of actual chamber.*

The use of an arrangement which yields comparatively large ionization currents eliminates many of the problems often met with in constructing ionization chambers. Insulation of moderate quality is sufficient since small leaks will be an extremely small percentage of the total current. Extreme care in cleaning the inner surface of the chamber is not necessary since the usual small radioactive contamination on metals is negligible. In addition all trouble from increased conductivity of insulators, as reported by Guében [2] when exposed to strong gamma radiation is eliminated since these variations are also insignificant in comparison with the main ionization current.

The complete arrangement is indicated in the diagram shown in figure 3. In this, the ionization chamber, C, is supplied with a voltage sufficient to produce saturation by the battery,[3] B. The insulated section of the central electrode is connected by a long paraffin-filled tube, with wire along its axis, to a 2-stage vacuum-tube amplifier described elsewhere.[4] The resistance, R, may conveniently be 10^8 ohms. The only other significant change in the amplifier from that described in the reference, is the introduction of a potentiometer, P, and a provision for compensating the *IR* drop in the resistance, R, so that a null method may be used, the microammeter, M, serving only to indicate the balancing of the drop in R. The method of use is made clear by a description of the procedure in making a measurement. With no radium in the chamber and the millivoltmeter reading 0, the microammeter, M, is adjusted to an arbitrary 0 by means of the rheostat, Rh. The radium is now put in the chamber and the microammeter, M, is brought back to the selected 0 by adjusting the reading of the millivoltmeter, V, until this is accomplished. The change in the potential difference across R produced by the ionization current resulting from introduction of the radium into the chamber is directly proportional to the reading of the millivoltmeter, V. This procedure permits all readings to be taken at this same value of the control grid potential of the first tube and thereby eliminates errors which would arise from changes in the control grid current when using the deflections of the microammeter, M, to measure the ionization current. The potentiometer, P, is used to provide a control grid bias such that the first tube operates on linear portion of its

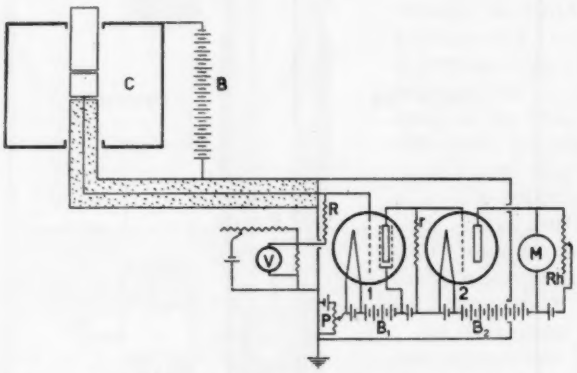

FIGURE 3.—*Diagram showing complete assembly for making gamma-ray comparisons of radioactive preparations.*

[2] Guében, G., Ann. Soc. Sci. de Bruxelles, vol. 49, p. 12, 1929.

[3] This voltage was obtained by a transformer and rectifier with simple filter circuit from the alternating-current supply. Live voltage fluctuations caused no detectable fluctuation of meters in output circuit of the amplifier.

[4] Curtiss, L. F., B.S. Jour. Research, vol. 10, (RP550) p. 583, 1933.

characteristic curve and is not changed once the desired point has been found. When a new tube is put in the circuit, it is usually necessary to redetermine the correct bias. The writer has found that a great deal of the annoying fluctuations frequently encountered when using ordinary radio tubes in a circuit as described above, arise in the molded base of the tube and that even when using a tube with control grid brought out of the top it is quite essential to remove the base for steady operation. Considerable improvement of behavior is also obtained by painting the outside of the tube to within several millimeters of the portions where leads are brought through the glass with a conducting paint. This coating is grounded. "Spray tubes" might serve equally well.

A factor which contributes to the speed and accuracy of this method is that all preparations, regardless of strength, are measured in the same position. This is of importance where many preparations of widely different radium content are being measured. Errors and delays arising from adjusting a radium holder to the proper distance from the electroscope are eliminated.

III. PRECISION OF METHOD

Since this arrangement is intended to take the place of a gold-leaf electroscope in standardizing radium preparations by the gamma-ray method, it is desirable to submit some evidence regarding its precision and reliability in comparison with the electroscope. This can be done most conveniently by table 1 which shows the results obtained from all readings taken on a set of 5 radium preparations contained in platinum tubes with walls 0.3 millimeters thick using the same radium standard, sealed in glass, for reference. These results are typical of a large number of comparisons which have been made between the two methods.

TABLE 1

Electroscope	Ionization chamber	Electroscope	Ionization chamber	Electroscope	Ionization chamber
Preparation no. 20728		Preparation no. 20730		Preparation no. 20732	
10.00	9.87	9.70	9.75	10.00	9.86
9.90	9.88	9.75	9.64	9.95	9.86
9.95	9.88	9.70	9.65	9.95	9.86
9.80	9.87	9.70	9.67	9.95	9.86
9.90	9.89	9.75	9.67	9.86	9.86
9.80	9.87	9.70	9.70	9.90	9.89
Average 9.89	*9.88*	*9.72*	*9.68*	*9.93*	*9.86*
Probable error ±.022	±.002	±.007	±.008	±.013	±.004
Preparation no. 20729		Preparation no. 20731		Preparation no. 20733	
9.56	9.52	10.05	9.86	10.04	10.01
9.70	9.52	9.90	9.90	10.10	10.01
9.66	9.52	9.95	9.89	9.99	9.99
9.60	9.51	9.86	9.88	9.99	10.01
9.51	9.54	9.80	9.89	9.94	9.99
9.46	9.52	9.80	9.89	9.94	9.99
Average 9.58	*9.52*	*9.89*	*9.88*	*10.00*	*10.00*
Probable error ±.024	±.002	±.024	±.004	±.017	±.002

From a study of the above table, it is evident that the systematic errors between the two instruments do not lie outside the accuracy usually claimed in the measurement of commercial radium preparations, that is, 0.7 percent. From the probable errors computed for each set of observations, it is also clear that the accuracy of the individual readings with the ionization chamber considerably exceeds that of those made with the electroscope. This increased accuracy can be used to reduce the number of observations required to obtain measurements of the required precision, and it has been found that three readings with the ionization chamber give results comparable in accuracy with those obtained from 18 individual readings on the electroscope.

The results given in the table also serve to show that the absorption correction for the ionization chamber is the same as for the electroscope. Any difference would appear as a systematic deviation in the results obtained by the two methods. Numerous measurements on a variety of types of preparations have failed to show any such deviation.

Since fewer readings are required to obtain results of the same accuracy, measurements can be made with the ionization chamber in about one tenth the time required with the electroscope. Furthermore, the reduction of readings to milligrams of radium is less laborious than for the electroscope since the readings of the millivoltmeter are directly proportional to gamma radiation of the preparations. The natural ionization is compensated in the zero setting of the microammeter. Thus the total saving of time afforded by the ionization chamber method is considerable.

The writer wishes to acknowledge the cooperation of G. W. Gardiner who suggested the design of chamber described, and of A. V. Astin, for help in eliminating some of the difficulties encountered. He is also pleased to acknowledge the help of L. L. Stockmann and B. W. Brown in constructing the parts of the chamber and amplifier.

WASHINGTON, October 25, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP642

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

A SEDIMENTATION METHOD FOR THE DETERMINATION OF THE PARTICLE SIZE OF FINELY DIVIDED MATERIALS (SUCH AS HYDRATED LIME)

By Dana L. Bishop

ABSTRACT

This paper reports a comparison between a sedimentation method of determining particle size distribution and a microscopic method and also some data on hydrated lime. Glass spherules were prepared from pyrex glass and fractionated so that most of the particles had a diameter within 2 microns of the average diameter of the fraction. These particles were then dispersed in a liquid and weighed as they settled out of suspension with an automatic-weighing device. From this sedimentation record the particle size distribution was calculated. The same sample was then used to determine the particle size distribution by measuring the diameters of several hundred particles with a microscope. In making the microscopic measurements the glass spherules were mounted in liquids of various refractive indices and it was found that differences in refractive index of the mounting medium produced appreciable changes in the apparent diameter (more than 20 percent in some cases). The microscopic and sedimentation measurements showed similarly shaped distribution curves but there was some variation between them. Particle size distributions of hydrated lime are also reported.

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I. INTRODUCTION

The fine particles of many finely divided materials are so small that it is impractical to make effective size separations by pneumatic methods and microscopic methods are not readily applicable. Since a knowledge of the particle size of hyrdated lime, portland cement, and many other substances may assist in explaining some of their properties, it was considered advisable to attempt to apply a method devised by Oden [1] to determine the particle size distributions of hydrated lime. Oden showed that a mathematical analysis involving Stokes' equation [2] for the fall of bodies through a viscous medium, will give a

[1] Proc. Roy. Soc. of Edinburgh, vol. 36, pp. 219 to 236, 1915.
[2] G. G. Stokes, Mathematical and Physical Papers, vol. III, p. 59, Cambridge University Press, 1901. Stokes' original equation was developed for kinematic viscosity.

fineness distribution provided the finely divided material is weighed as it settles out of suspension.

Arnold [3] found that individual spheres as small as 130 microns in diameter fall in a viscous medium with a velocity corresponding to that given by Stokes' equation. However, since the particles of many materials such as hydrated lime are very much smaller than the individual spheres used by Arnold, a study was made to ascertain the accuracy with which the particle size distribution could be determined by Oden's method.

Hydrated lime in itself is not a particularly suitable material for this purpose since the particles are irregular in shape and therefore very difficult to measure microscopically. Accordingly the performance of the weighing device was studied with the use of carefully prepared fractions of glass spherules whose diameters could be more readily investigated microscopically. This paper deals therefore with the comparison of the particle size distributions of fractions of glass spherules as ascertained with the sedimentation apparatus, with that determined microscopically. It also contains some data on hydrated lime to show in general the particle size distribution of this material. Just how this factor may be related to other properties of hydrated lime is being investigated.

II. THEORY OF SEDIMENTATION METHOD

In the following discussion, "distribution curve" [4] means the relation between the percentage of material and the corresponding diameters. A "cumulative curve" shows the amount of material which is coarser than a given size. When a fine material is uniformly dispersed in a liquid and allowed to settle, the curve showing the weight of material settled out as a function of time is a "sedimentation curve."

A distribution curve may be obtained from a sedimentation curve in the following manner.[5] The amount of material, P, settled on the pan at a given time consists of two parts; one part S, made up of all the particles coarse enough to have settled the entire length of the column, and a second part, consisting of those particles of smaller size which, though they may not have settled the full length of the column, have nevertheless reached the pan. Each size of this second part has a constant settling velocity and the rate of their accumulation on the pan may be represented as $\frac{dP}{dt}$. At time t, the weight of this second part, amounts to $t\frac{dP}{dt}$. The total weight, P, settled at time t, is therefore,

$$P = S + t\frac{dP}{dt} \tag{1}$$

[3] Phil. Mag., series 6, vol. 22, pp. 755-775, 1911. In "The Electron", University of Chicago Press, 1929, Millikan states that Arnold obtained results which agreed with Stokes' equation for particles having diameters as small as 40 microns.

[4] F. C. Mills, Statistical Methods. Henry Holt & Co., New York, N.Y., 1924.

[5] T. Svedberg, Colloid Chemistry, Chemical Catalog Co., 1924.

If for a given time, corresponding to a certain diameter calculated from Stokes' equation, a tangent is drawn to the sedimentation curve, figure 1, the intercept W on the ordinate will be $W=P-t\frac{dP}{dt}$, but from (1) $S=P-t\frac{dP}{dt}$.

Therefore, $W=S$. Since S is the coarse part of the sediment, the intercept of the tangent divides the sediment into that amount which is coarser than a certain size and an amount finer than that size. The size corresponding to a given time is determined from Stokes' equation:

$$V=\frac{(\rho-\rho')gd^2}{18\eta} \tag{2}$$

in which V is the velocity of a particle falling through a viscous medium, ρ the density of the particle, ρ' the density of the medium g the acceleration of gravity, d the diameter of the particle, and η the coefficient of viscosity of the medium. If W, after being reduced to a percentage basis, is plotted against size, an accumulation curve is obtained from which a distribution curve is derived by plotting the ordinate intercept of equal units of diameter against particle size.

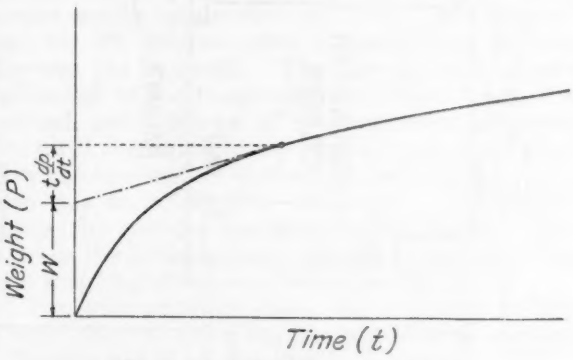

FIGURE 1.—*Sedimentation curve.*

III. DESCRIPTION AND OPERATION OF SEDIMENTATION APPARATUS

The apparatus with which sedimentation curves were obtained is illustrated in figure 2. The material being analyzed is thoroughly dispersed in a liquid and introduced into the sedimentation cylinder. As the particles settle on the pan attached to the left arm of the balance, the beam is rotated counterclockwise, thus deflecting the image of the lamp from the opaque screen onto a photoelectric cell. This causes an increased current to flow, which, after being amplified by the vacuum tube, operates the relay to start the motor connected with the drum resistance. The motor runs until enough resistance is cut out to increase the solenoid current sufficiently to restore the equilibrium of the balance and throw the light off the photoelectric cell. This is repeated automatically for each effective increment of weight produced by the material settling from suspension. A record of the current flowing through the solenoid circuit then corresponds to a time-weight record of the sedimentation of the sample.

The balance was inclosed in a double-walled cabinet provided with an air circulating system. A heater placed in the circulating system was regulated by means of a grid type toluene regulator in conjunction

with a vacuum tube control similar to the device of D. J. and J. J. Beaver.[6] The temperature within the balance case, as indicated by a single thermometer, was maintained at 30.0 ± 0.05 C.

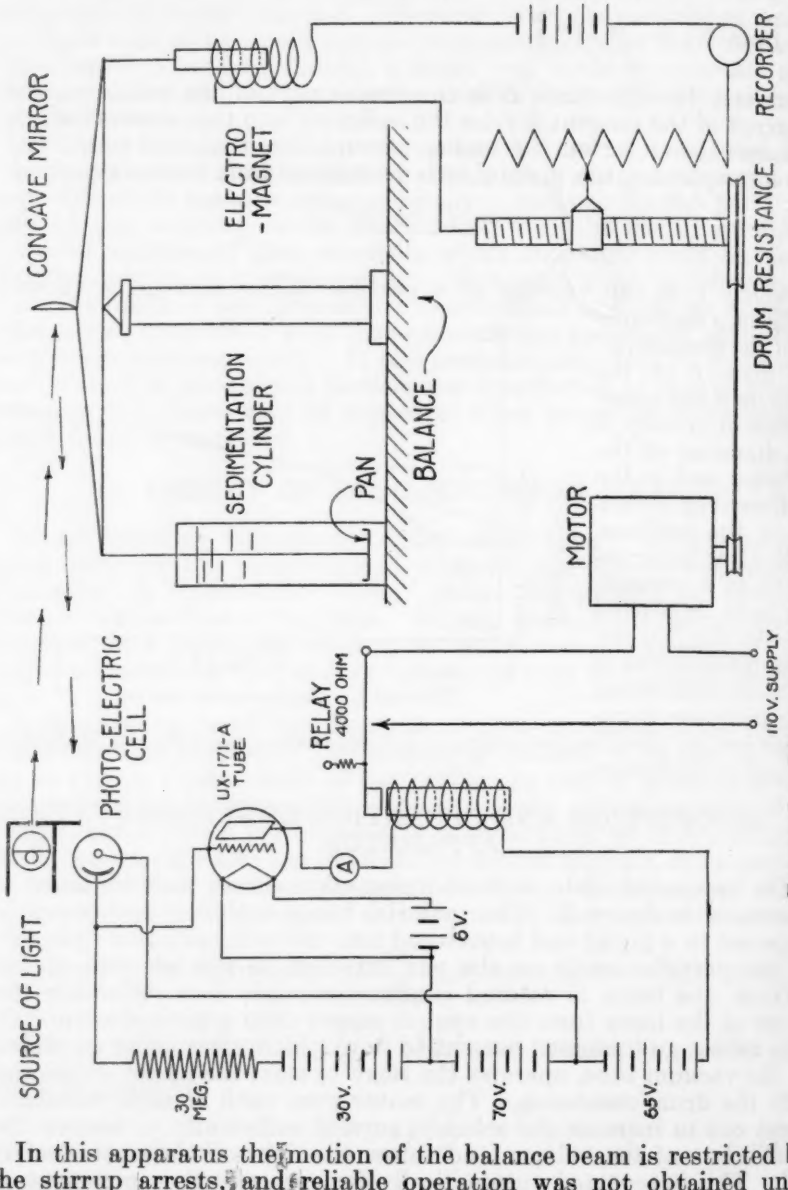

FIGURE 2.—*Diagrammatic sketch of automatic weighing apparatus.*

In this apparatus the motion of the balance beam is restricted by the stirrup arrests, and reliable operation was not obtained until agate bearing stirrup arrests were used.

A concave mirror having a focal length of 35 cm and a diameter of 8 cm was attached to the balance beam at its axis of rotation. The magnet attached to the right end of the beam was of cobalt-magnet steel which was annealed before being magnetized.

[6] Jour. Ind. Eng. Chem., vol. 15, pp. 359–361, 1923.

In order to measure the current in the solenoid circuit, a recording potentiometer was used to measure the drop in voltage at the potential terminals of a suitable shunt. The potentiometer was a double range instrument and the shunt so chosen as to use nearly its entire range. A 50-cm scale was thus available on which to record the current. The entire scale was calibrated by adding weights to a supplemental balance pan above the liquid and between the balance beam and the sedimentation pan. The system was found to be accurate to about 0.2 mg.

The drum resistance in series with the solenoid was made by winding no. 20 advance wire in a groove on a hard-rubber drum. A transparent celluloid cover was provided for the drum resistance to protect it from dust, but it was necessary to clean the wire occasionally with vaseline.

To obtain a sedimentation curve, the material to be analyzed was placed in the sedimentation cylinder and butyl alcohol added to bring the level of the suspension nearly to a prescribed level. The suspension was then agitated for 30 minutes with a mechanical stirring device in order to disperse the material. The temperature of the suspension was next adjusted to the temperature of the cabinet, the sedimentation pan inserted, and the level of the suspension adjusted by adding butyl alcohol until the liquid just touched a wire suspended a definite distance below the top surface of the cylinder. (The depth of the liquid to the pan was either 21.7 or 10.85 cm). Meanwhile segregation was prevented by moving the pan up and down. The cylinder was then placed in the balance case, the pan attached to the beam and the automatic weighing device started immediately.

In the reduction of the sedimentation data, the tangents to the sedimentation curves were calculated by the method of least squares as developed by F. T. Gucker and H. J. Brennen.[7]

IV. PREPARATION AND MICROSCOPIC MEASUREMENTS OF GLASS SPHERULES

In order to make a comparison between the microscopic and sedimentation methods it was desirable to have a material whose dimensions could be measured microscopically with considerable accuracy. Such a material was made by grinding pyrex glass in a steel ball mill. Most of the adventitious iron was then removed with a magnetic separator and the remainder by treatment with dilute hydrochloric acid and distilled water. The powdered glass was then dried and introduced into the air line of a blast lamp.[8] The glass fused while passing through the flame and assumed a spherical shape, as is shown by the photomicrographs (fig. 3). Repeated fractional sedimentations in ethyl alcohol were made and finally four fractions, each of which had a small range of sizes, were obtained. A portion of each of these four fractions was weighed and combined to make a composite sample.

In order to obtain distribution curves for comparison with the sedimentation method, the particle size of each fraction was determined microscopically. For this purpose a microprojector was used

[7] Jour. Am. Chem. Soc., vol. 54, pp. 886-888, 1932.

[8] The author is indebted to F. G. Cottrell and C. G. Gilbert for this method of preparing the glass spherules.

in which the light from an arc lamp, after passing through a water cell and an abbé condenser, was sent through a microscope and projected onto a screen. The magnification, obtained with a 4 mm objective, was about 2,600 diameters and with a 1.9 mm immersion objective, about 5,700 diameters, determined by projecting a 100 micron interval of a calibrated stage micrometer on a screen. The projected field was examined with 10-micron intervals and only the undistorted portion of the field was used when measuring the diameters of the spherules.

The effects of changes in adjustments of the microscope were investigated by measurements on a number of particles. If the focus on a particle was changed so that the Becke [9] line appeared either outside or inside the particle, no change in diameter could be detected. Changing the diaphragm opening and lowering the abbé condenser several millimeters had no appreciable effect on the observed diameter. Although these changes produced no measurable effects, all measurements were made under similar conditions, the microscope always being focused so that the Becke line just disappeared.

The particle size distribution of each fraction was determined on the material removed from the sedimentation apparatus. For this purpose the fraction was thoroughly dispersed in the butyl alcohol and a small quantity placed on a microscope slide. A cover glass was put on and worked over the suspension until nearly all the alcohol had evaporated. The cover glass was then removed and the residual alcohol evaporated. A mounting medium of known refractive index was then put on the slide and the cover glass worked around until an evenly dispersed layer of particles was obtained. Under the microscope these particles appeared well defined, making it possible to accurately measure their apparent size. The diameter of each particle was measured to one-quarter micron and the particles were classified in half-micron intervals. When the mean diameters of different groups of about 100 particles each were calculated, good agreement was obtained provided the particles were always mounted in the same mounting medium. For example, the mean of six such groups (measured from three slides by three observers) was 6.07 microns with a standard deviation of 0.09 micron. Although this agreement held when changes in mounting media were made, the apparent diameter changed with change in mounting medium, as is shown in figure 4 where the arithmetic mean particle size is plotted against refractive index of the mounting medium. Measurements were not made in mounting oils having indices between 1.52 and 1.42 because of the low relief in such oils. (The refractive index of the glass was 1.47.) Since each point represents the arithmetic mean diameter of from 200 to 400 particles and the same order of change occurs in all three fractions, it is hard to account for these differences as observational errors.

Measurements were also made on individual spherules by means of a filar micrometer. A permanent mounting of glass spherules was obtained by heating a microscope slide, to such a temperature that the spherules fused to the slide and yet did not become imbedded to any appreciable extent. Scratches on the slide, made with a glass cutter, aided in finding a given field. Individual particles in a field

[9] A. N. Winchell, Elements of Optical Mineralogy, part I, p. 70, John Wiley & Sons, 1928.

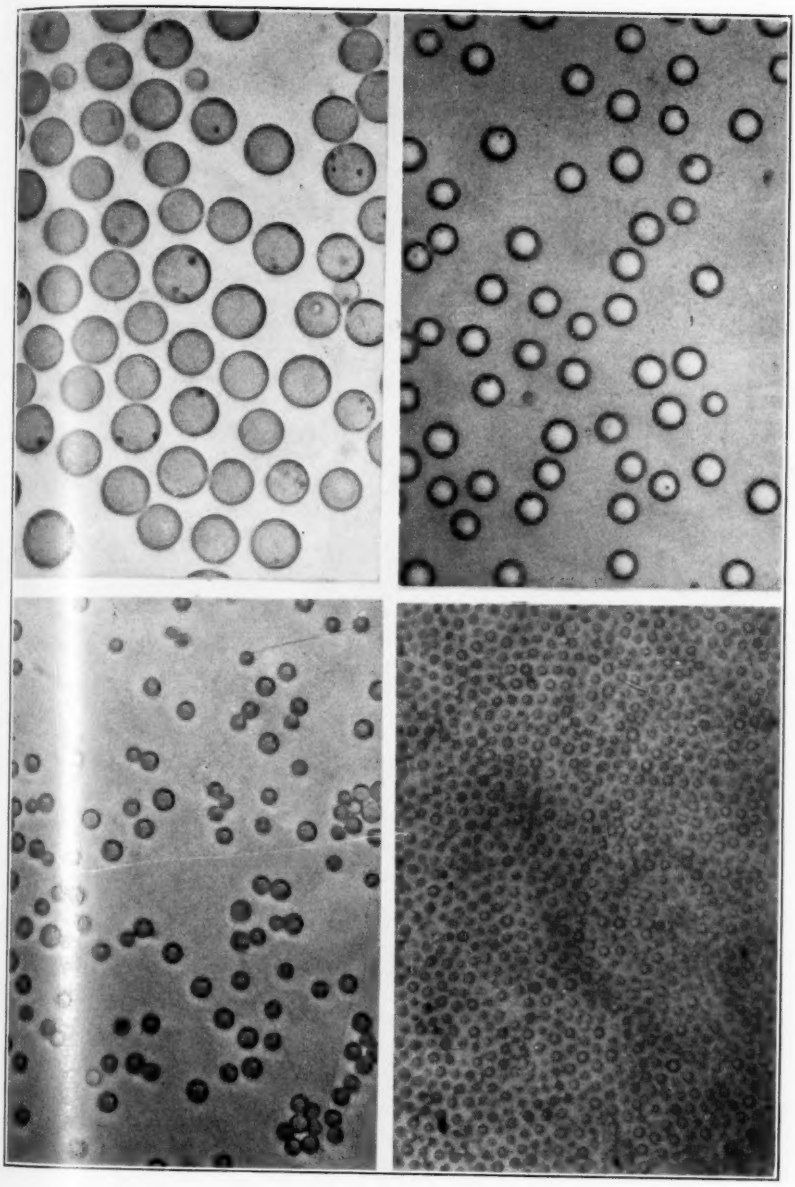

FIGURE 3.—*Photomicrographs of the four fractions of glass spherules.*
(All magnified 700 diameters.)

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could be identified and measurements were made on these particles when immersed in mounting media of various refractive indices. These measurements are also shown in figure 4. The standard deviation of each of these points is considerably less than 0.1 micron. The order of variation is the same as was found on the fractions of glass spherules. Measurements made with and without critical illumination did not change the results.

It appears, therefore, that in making measurements of particle size with a microscope, there must be taken into account the effect

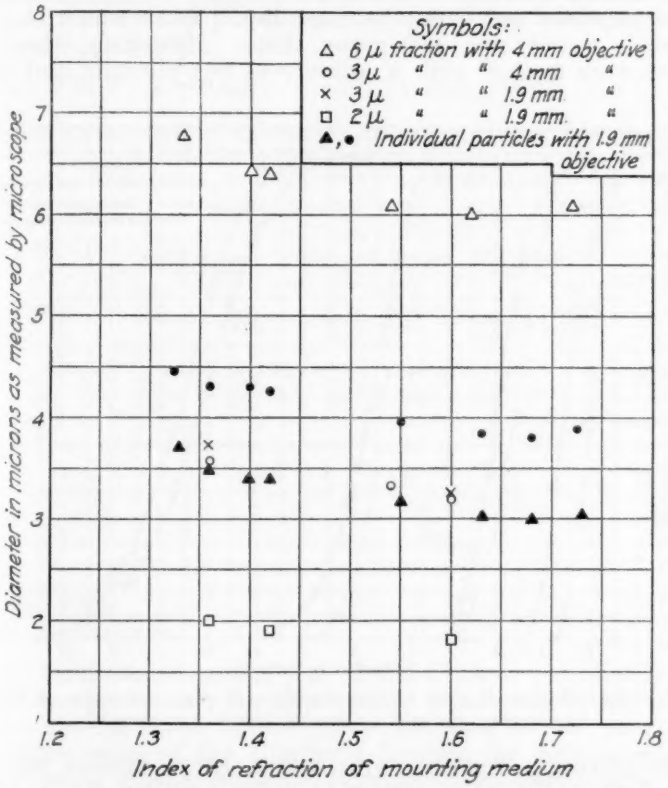

FIGURE 4.—*Effect of change in index of refraction of mounting medium on microscopic measurements of diameters of glass spherules* (N_d=1.47).

produced by the mounting medium. Although this phenomenon has been reported in the literature,[10] many investigators have not considered its effect when measuring particle size. No other method was used to determine the true particle size distribution of the fractions and this paper, therefore, reports only a comparison between the microscopic and sedimentation methods. The microscopic distributions chosen are an average of measurements made in mounting media whose indices were approximately 1.40 and 1.60. These values were arbitrarily chosen but it is not known whether or not this gives true particle size.

[10] For instance W. Marshall mentions this change of size in "The Influence of Refractive Index on Mounting Media", Jour. Roy. Mic. Soc., vol. 52, pp. 275–280, 1932.

V. DISPERSION OF GLASS SPHERULES FOR SEDIMENTATION

The accuracy of any sedimentation method will depend largely upon having the sample of the particulate material completely dispersed. Two sources of difficulty were experienced in dispersing these fractions of glass spherules. It was found that whenever a dispersion medium was allowed to evaporate from the glass spherules they caked together and dispersed again only with difficulty. Apparently a minute quantity of material, left on the surface, bound the particles together and even the same liquid from which they were evaporated would not redisperse them. However, when these spherules were treated with a mixture of hot chromic and sulfuric

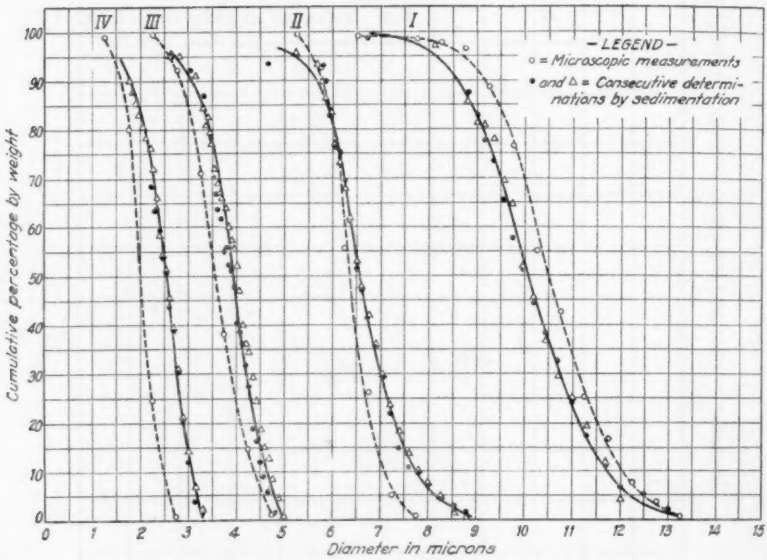

FIGURE 5.—*Distribution of sizes of four fractions of glass spherules as determined by microscopic and sedimentation measurements.*

acids, followed by washing with water, ethyl alcohol and butyl alcohol, better dispersion was obtained. Another source of difficulty occurred after the spherules had been kept in butyl alcohol for a long time. In weighing portions of the four fractions to make the composite sample, it was noticed that a film of organic material remained on the glass spherules after evaporation of the butyl alcohol. This film was readily removed by treatment with a mixture of hot chromic and sulfuric acids. Better dispersion was obtained after treatment with these acids than before the treatment, as was indicated by better agreement of the mean values and standard deviations with the corresponding measures of the microscopic data. All the sedimentation results reported in this paper were obtained on fractions which had been given this acid treatment.

VI. COMPARISON OF MICROSCOPIC AND SEDIMENTATION MEASUREMENTS

The results of the microscopic and sedimentation measurements are given in figures 5 and 6 in which cumulative percentages are plotted against particle size. The data of figure 5 and the calculated surface values are also summarized in table 1. The reduction of the sedimentation data gives a distribution by weight and the microscopic measurements were, therefore, calculated to a weight basis.[11] The cumulative curves of the sedimentation data were obtained by the method previously outlined by using the following numerical values in equation (2):

$$\rho = 2.21,^{12} \quad \rho' = 0.804, \quad \eta = 0.0231 \text{ and } g = 980 \text{ (cgs units)}$$

TABLE 1.—*Comparison of microscopic and sedimentation determinations of the particle size of four fractions of glass spherules*

Fraction no.	Weight distribution				Surface distribution			
	Mean diameter		Standard deviation		Mean diameter		Surface per gram	
	Microscopic $\frac{\Sigma nd^4}{\Sigma nd^3}$	Sedimentation $\frac{\Sigma n'd}{\Sigma n'}$	Microscopic $\sqrt{\frac{\Sigma nv^2}{\Sigma n}}$	Sedimentation $\sqrt{\frac{\Sigma n' v^2}{\Sigma n'}}$	Microscopic $\frac{\Sigma nd^3}{\Sigma nd^2}$	Sedimentation $10^{-2}\Sigma\frac{\frac{n'}{d}}{\Sigma\frac{n'}{d}}d$	Microscopic $\frac{6\times10^4}{\rho d'}$	Sedimentation $\frac{6\times10^4}{\rho d'}$
	μ	μ	μ	μ	μ	μ	cm^2/g	cm^2/g
I	10.7	10.1	1.27	1.21	10.5	9.9	2,590	2,730
II	6.5	6.6	.50	.86	6.4	6.5	4,240	4,160
III	3.7	3.9	.54	.59	3.6	3.8	7,600	7,200
IV	2.1	2.5	.41	.45	2.0	2.4	13,400	11,300

d=midpoint of class.
n, n'=class frequency.
v=deviation from mean.
d'=surface mean diameter.

These cumulative curves (figs. 5 and 6) show a similarity of shape for the two methods. For all fractions this similarity holds, not only for the general shape of the curves but also for the range of sizes. The mean value of the 10-micron fraction, as determined by sedimentation, is smaller than the microscopic determination, while for the three smaller fractions the sedimentation values are greater than the microscopic values. These deviations produce a difference of about 6 percent on the calculated surface of the 10-micron fraction, 2 percent on the 6.5-micron fraction, 5 percent on the 3.5 and on the 2-micron fraction 16 percent.

Since it was not determined which refractive index of mounting medium will give true particle size when glass spherules are measured with a microscope, no attempt has been made to explain the differences found or to obtain better agreement between sedimentation and microscopic data.

Coutts and Crowther,[13] and Shaw and Winterer [14] reported that, under certain conditions, the percentage of material settling on a

[11] Perrot and Kinney, Jour. Am. Ceram. Soc., vol. 6, pp. 417–439, 1923.
[12] The density of the powdered glass from which the spherules were made was 2.25.
[13] Trans. Farad. Soc., vol. 21, pp. 374–380, 1925.
[14] Int. Cong. of Soil Science, vol. 1, pp. 384–393, 1927.

pan suspended in a disperse system is not proportional to the relative area of the pan and the cross-sectional area of the container. In the current investigation some of the 6-micron fraction (which had been kept in ethyl alcohol) was dried, weighed, and redispersed in the sedimentation cylinder. At the end of 48 hours 167 mg had settled on the pan, whereas the calculations indicated that 168 mg should have been recorded. After a sedimentation of the 10-micron fraction, the material settled on the pan and also that which settled on the bottom of the cylinder were carefully removed and their particle sizes determined microscopically. The arithmetic mean diameter of 900 particles of the material collected on the pan, was 9.84 microns, and the corresponding value of 869 particles from the bottom of the cylinder, was 9.81 microns. Since this difference is of no significance it is believed that the material settling on the pan was representative of all the material placed in the sedimentation cylinder.

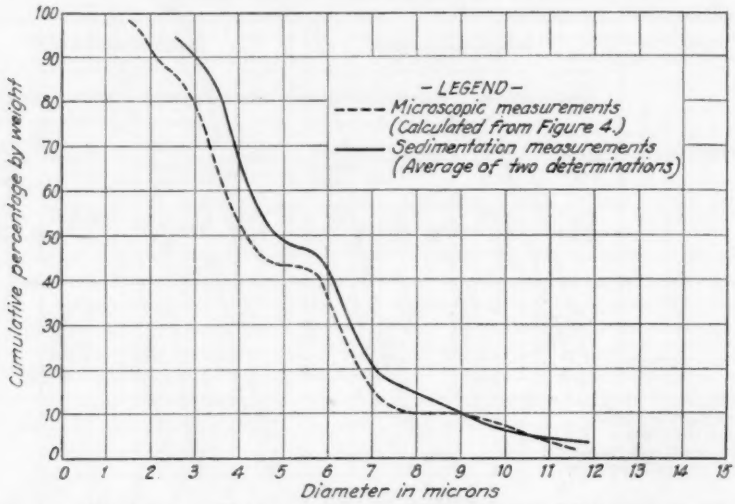

FIGURE 6.—*Distribution of sizes of a composite sample containing portions of the four fractions shown in figure 3.*

VII. PARTICLE SIZE OF HYDRATED LIME

Although it has not been demonstrated that the sedimentation apparatus gives true particle size, the error involved is probably not too great for an initial study of the relation between particle size and other properties of lime. Sufficient limes have not been studied so far to be able to correlate particle size with other properties but there is included a table showing the particle size of a few limes in order to show the range of sizes encountered in commercial hydrated limes. The indicated diameters in the table were calculated from Stokes' equation and are therefore the diameters of spheres having the same settling velocity and density (2.3 for high calcium hydrates and 2.5 for dolomitic hydrates) as the lime particles.

TABLE 2.—*Particle sizes of nine hydrated limes*

Diameters	Percentages coarser than given size								
	High calcium hydrates, sample numbers					Dolomitic hydrates, sample numbers			
	1	2	3	4	5	6	7	8	9
μ	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
40	6	-------	5	2	2	6	15	8	12
30	9	1	6	3	3	9	20	11	17
20	13	2	9	8	6	13	27	20	22
10	25	10	20	30	27	35	40	35	38
5	70	55	55	80	68	81	65	58	62
3	90	80	81	94	92	-------	-------	85	86

VIII. CONCLUSIONS

Microscopic measurements on glass spherules have shown that changes in refractive index of the medium surrounding the particle alter the apparent diameter of the particle. The magnitude of this change is such that until it is known which refractive index will give true particle size, the microscope certainly has limited use as a means of determining particle size. When fractions of these glass spherules were well dispersed in butyl alcohol, fair correlation of particle size distribution was obtained between sedimentation measurements and an average of microscopic measurements. Since this correlation was obtained, the sedimentation method was considered sufficiently accurate to make particle size measurements of hydrated lime.

WASHINGTON, October 28, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP643

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A CRITICAL TEST FOR THE PURITY OF GASES

By Martin Shepherd

ABSTRACT

This paper reports a method by which the purity of gases (and liquids having normal boiling points below room temperatures) may be critically tested. The method involves one approximately isothermal distillation, whereby a small initial distillate, a middle cut, and a small final residue are obtained. The pressures of these three fractions are intercompared by means of a simple differential manometer and form the basis for indicating impurities of higher and lower boiling points than that of the approximately pure substance.

The method eliminates the exacting temperature requirements of the widely used criterion of constancy of pressure during an isothermal condensation or vaporization. At the same time, it offers more information than the isothermal condensation, and is suitable for testing mixtures containing more than two components. In many cases the order of magnitude of the impurities may be calculated. Like the isothermal condensation, it is not suitable for studying azeotropic mixtures.

The preparation of a pure gas is not an easy matter, and satisfactory tests for purity are often difficult to formulate and usually difficult to perform. In many cases the method of preparation is about as good a guarantee of purity as the method of test subsequently applied, and sometimes it offers even more reliable assurance of purity. These complications are largely responsible for the fact that reported investigations deal abundantly with gases of doubtful purity.

The ordinary methods of so-called "exact" volumetric gas analysis, which are often employed in the effort to establish the purity of a gas, are subject to errors of such magnitude as to be unfit for this purpose. It is sometimes possible to design very special chemical methods which may offer satisfactory evidence of purity. In general, however, the measurement of one or more of the physical properties of a gas affords the basis for the determination of its purity.

One of the most frequently employed criteria for purity is the constancy of pressure during isothermal condensation or vaporization. The method is very useful, but has limitations which are not generally recognized. Washburn [1] has discussed the physical limitations of this method.

In this connection, Washburn suggested a more sensitive and convenient method for determining purity in case the substance to be examined is nearly pure. This suggestion is given on page 595 (paragraph 3) of his paper, and forms the basis of the method described in the present discussion. The apparatus and detailed technique, which have been found suitable for the application of this method, are reported in order to make the method easily available. At the same time, the original suggestion has been extended in order to permit the collection of additional information.

[1] E. W. Washburn, Constancy of pressure during isothermal condensation or vaporization as a criterion of purity, Zs. physik. Chemie (Cohen-Festband), p. 592, 1927.

One of the exacting demands of the method of isothermal condensation is the required maintenance of very constant temperatures over relatively long periods. An elaborate cryostat is consequently necessary. It is a relatively simple matter to avoid this difficult requirement, and at the same time to improve greatly the sensitivity of the test for purity. Furthermore, it is possible to extend the information obtained by establishing the presence or absence of impurities having boiling points both higher and lower than that of the approximately pure substance. The identity of these impurities can sometimes be established, and if the mixture is limited to three components, the order of magnitude of the amounts present may be determined in many cases.

The method is as follows. One simple approximately isothermal distillation is conducted. The vapor pressure of a very small portion

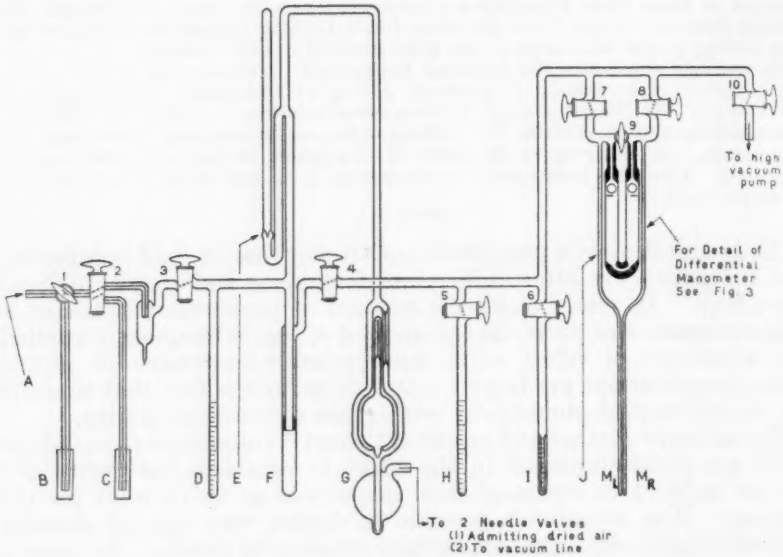
To high vacuum pump
For Detail of Differential Manometer See Fig. 3
To 2 Needle Valves (1) Admitting dried air (2) To vacuum line

FIGURE 1.—*Assembly of apparatus.*

of the initial distillate is compared differentially with that of a small portion of the middle cut, and the vapor pressure of the latter fraction is in turn compared differentially with that of the small final residue. The method retains one of the limitations of the isothermal condensation, in that it is not suitable for azeotropic mixtures. Another limitation is that the approximately pure substance condense (at pressures not greatly exceeding atmospheric) at temperatures ordinarily available. The practical lower limit in most laboratories would be about −210 C (liquid air boiling under reduced pressure).

The apparatus required is not extensive and can be constructed more easily than a good cryostat. The assembled unit is illustrated in figure 1.

The procedure is best followed by referring to this diagram. The whole apparatus is thoroughly evacuated until no pressure increase is indicated by the McLeod gage, G, after the mercury vapor pump has been shut off at cock 10 for several hours.

The gas sample to be tested is introduced at A. The arrangement of stopcocks 1 and 2 and mercury seals B and C permits necessary variations in the method of transferring the sample. The sampling connections may be flushed with gas or mercury through C. The seal B acts as a manometer to insure positive pressure (if desired) during the transfer, and also provides a safety outlet if the sample is stored under pressure. If the sample container is sealed to A, the connections may be evacuated. The amount of sample and method of storing will determine the desirable procedure.

The sample is condensed in the graduated tube D. The amount to be condensed will depend upon the volume of gas available for the test, and, if a sufficient amount is at hand, two or three ml of condensate may be taken. The volume of the condensate is noted at the condensing temperature. The same temperature should be used subsequently for condensing the small fractions in the differential manometer. Liquid air is often convenient for this purpose, although solid carbon dioxide or other suitable cooling agents are sometimes required.

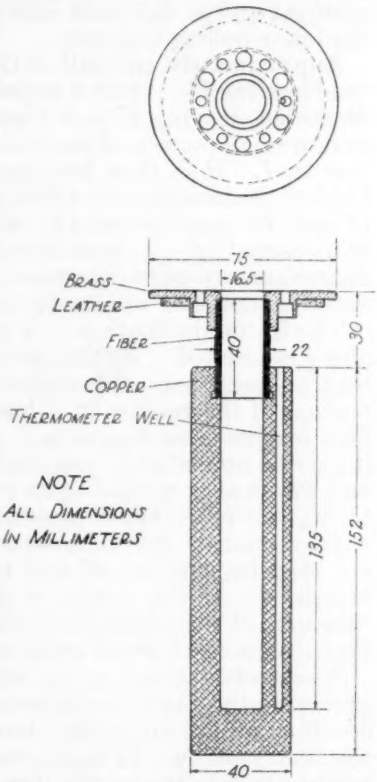

FIGURE 2.—*Detail of metal envelop for distilling tube.*

The condensate is next transferred (by vaporizing and condensing) to the distilling tube *F*. Its pressure (measured by the barometric manometer *E*) at liquid-air temperature may sometimes indicate a nitrogen or air impurity in a substance whose vapor pressure is very low at this temperature. The distilling tube is now surrounded by a snugly fitting copper block (fig. 2) adjusted to the proper temperature for the approximately isothermal distillation. This metal envelop is suspended in a dewar tube and cooled to the desired temperature. It has sufficient heat capacity to maintain this temperature with little attention. The distillation should be conducted at low pressures (the order of a few mm). A thorough discussion of the procedures employed for this type of distillation is given in a previous report.[2]

The initial distillate is condensed in the graduated tube *I* at the temperature previously used to condense the entire sample (a temperature much lower than that of the distilling tube). Its volume is noted and compared with that of the total sample. The optimum volume of initial distillate (or final residue) is the smallest amount which can be transferred to the differential manometer with assurance

[2] Martin Shepherd, B.S. Jour. Research, vol. 2 (RP75), P. 1145, 1929.

that it will not be completely vaporized at the temperature employed for the measurement of vapor pressure differences. Greater sensitivity is thus obtained. This optimum may be determined from the approximate values for the capacity of the manometer above the condensate, the density of the liquid at the condensing temperature and the vapor pressure at the temperature used. When the proper amount of initial distillate has condensed in I, 4 is closed and 8 opened to transfer the distillate to the right-hand condensing bulb (M_R) attached to the differential manometer J. M_R is then isolated by closing 8. The vapor pressure of the initial distillate (within the range of the manometer) may now be measured. This measurement is optional and is desirable only in case it may indicate the nature of the lower boiling impurity.

Approximately one half of the condensate in F is now distilled and condensed in H. Cock 4 is closed and this fraction is pumped off and discarded, leaving H and I evacuated. The distillation is resumed until a small portion of the middle cut has been collected by condensation in I. It is then transferred to the left-hand condensing bulb (M_L) of the manometer, which is isolated by closing 7. The difference (if any) in vapor pressure between the initial distillate and middle cut is measured at a temperature near the normal boiling point of the approximately pure substance. The procedures for using the differential manometer will be discussed later.

The initial distillate is now discarded to the pump, leaving M_R, H, and I evacuated. At this point the vapor pressure of the middle cut may be measured. The distillation is again resumed until the major portion of the residue in F has been collected in H. The last small final residue is condensed in I. If its volume happens to be too large, it may be immediately transferred to F, another portion distilled to H and the smaller residue again collected in I. From I it is transferred to M_R, where its vapor pressure is compared with that of the middle cut by reading the differential manometer. If desired, the middle cut may be pumped off and the vapor pressure of the final residue measured. If the purity of the substance is very high, the vapor pressures of the initial distillate and final residue should be compared directly for the highest sensitivity.

A secondary check on the differential manometer may be made by observing the vapor pressures of the condensate in F, before and after distilling off the initial distillate and middle cut, and before removing the final residue. It is, of course, necessary to adjust the distilling temperature to the same value for these observations, and this cannot always be done precisely nor can proper equilibrium always be assured.

The differential manometer is shown in figure 3. Its construction is very simple. The positions of the mercury menisci are read by two hollow micrometer heads or gages (not shown in fig. 1) which are cemented onto the arms of the manometer. The rotating cylinders of these gages are engraved with vernier scales exactly as in an ordinary micrometer gage. The readings are taken in the same manner as with the better class of barometers. The manometer can be read to 0.01 mm. Since both arms are read, the limiting precision is about 0.02 mm, although the actual accuracy obtained will depend largely upon errors caused by differential capillarity. A 10 mm bore will meet the average requirement, although larger diameters are sometimes necessary. Results with oxygen, for example, indicated the inade-

quacy of the 10 mm size. If a systematic capillarity error is suspected, the relative positions of the condensates may be interchanged by transferring from M_R to I, M_L to M_R, and I to M_L.

The mercury is prevented from large accidental displacements by two check valves. These are simply spherical glass balls ground to seat against a conical grinding in the tube above.

The zero reading of the manometer is taken (before transferring any distillate) with both sides evacuated. Stopcock 9 or 7 and 8 should be opened. A check is made after adjusting the temperature around the condensing bulbs of the manometer. At the end of a determination, cock 9 may be opened to check the zero reading. (The use of cock 9 is optional. It is not shown in fig. 3.)

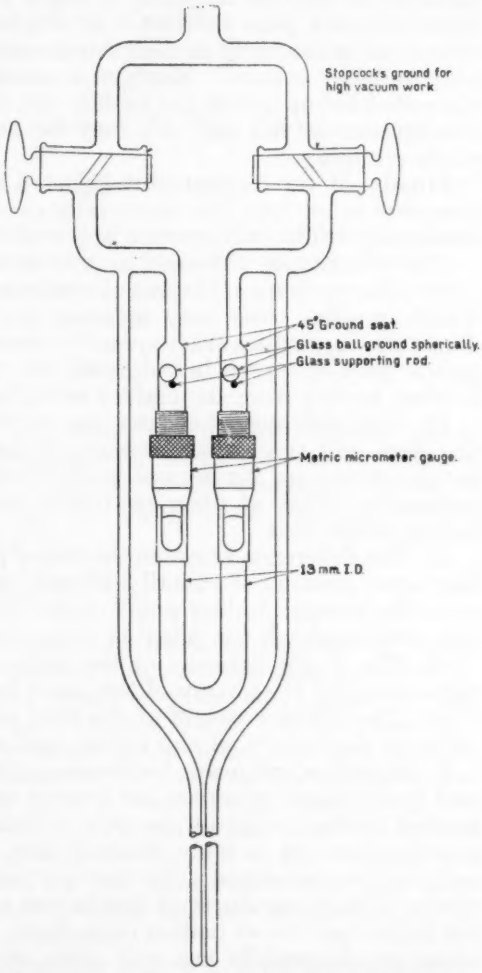

FIGURE 3.—*Detail of differential manometer.*

The entire accuracy of the differential vapor pressure measurement depends upon securing a very uniform temperature around the condensing bulbs of the manometer. The temperature need not be accurately measured, accurately adjusted to any fixed value, nor even be constant. But it must be the same around and in each condensing bulb. For this reason, the bulbs terminate at the same level and touch one another. Even so, it is often impossible to secure uniform temperature around them when they are immersed in a liquid bath even though it may be vigorously stirred. This difficulty was eliminated by surrounding the bulbs with a tube containing mercury, which freezes as a solid block around them at low temperatures. When this is done, the pressures remain quite steady and no fluctuations are observed. The mercury can be cooled as desired by liquid air which is added to the dewar tube surrounding M_L and M_R. This insulation prevents any sudden temperature change outside of the frozen mercury.

The precautions to be observed in using the differential manometer are simple. Enough condensate must be taken so that some liquid will be present at the temperature employed for the differential vapor pressure measurement. If too much condensate is taken, the surface

of the liquid may be above that of the surrounding mercury and the observed pressure will be too high. The error may be large in either of the two cases mentioned. If the prescribed technic is followed, the meniscii of the two condensates will be at the same level.

Another precaution which must sometimes be taken is to insure the removal of nitrogen or air from the middle cut and final residue. It is sometimes desirable to remove these impurities from the initial distillate, if their presence is satisfactorily established and the possible presence of another impurity of lower boiling point than that of the approximately pure substance is sought. For example, in testing a sample of propane, it is desirable to remove nitrogen in order to be able to detect ethane. Nitrogen is usually removed with the portion discarded before taking the middle cut, but in case of doubt, the small condensates in M_R and M_L may be held at liquid-air temperature while pumping.

Finally, if the temperature selected for the comparison of vapor pressures is too low, the manometer cannot be read with the required sensitivity. This will become apparent in the following discussion.

The information obtained may be listed:

(1) The pressure of the initial condensate at liquid air temperatures, which in some cases may indicate the presence of nitrogen or air. These two impurities are frequently present. Other gases of low boiling points, may, of course, be indicated, but the likelihood of their presence is often known from the history of the sample.

(2) The difference between the vapor pressure of a small initial distillate and the vapor pressure of the middle cut, measured at a temperature near the normal boiling point of the approximately pure substance. This at once establishes the possible presence of lower boiling impurities.

(3) The difference between the vapor pressure of the middle cut and the vapor pressure of a small final residue, measured at a temperature near the normal boiling point of the approximately pure substance. This will establish the possible presence of higher boiling impurities.

(4) The vapor pressure of the initial distillate, which may sometimes indicate the nature of the lower boiling impurity.

(5) The vapor pressure of the final residue, which may sometimes indicate the nature of the higher boiling impurity.

If the higher and lower boiling impurities are each single substances and their vapor pressures are known at some temperature near the normal boiling point of the pure substance, and if these impurities may be assumed to obey Raoult's law, the approximate amounts of each can be calculated. For this purpose, it will also be necessary to assume that the isothermal distillation achieved a sharp separation of the higher and lower boiling impurities, which will not always be true although the middle cut will often be free from lower and higher boiling impurities. If sharp separation was not attained, the calculation proposed will not indicate the maximum amount of impurity, but simply the difference in purity of the two fractions involved, from which it is possible to state there is at least a certain amount of the impurity present.

The expression by means of which the difference in purity between any two fractions may be calculated is derived from Raoult's law. Let A and B identify the substances of the two-component systems composing the fractions, p^o_A and p^o_B their respective vapor pressures

in the pure state, and X_A and X_B their mole fractions. Then, if p is the total vapor pressure of the mixture,

$$p = p^o_A X_A + p^o_B X_B = p^o_A(1 - X_B) + p^o_B X_B. \quad \text{(Raoult)} \tag{1}$$

Such an equation may be written for each fraction, the subscripts 1 and 2 identifying the two fractions:

$$p_1 = p^o_A(1 - X_{B_1}) + p^o_B X_{B_1}, \tag{2}$$

$$p_2 = p^o_A(1 - X_{B_2}) + p^o_B X_{B_2}. \tag{3}$$

The difference in the vapor pressures of the two fractions obtained by subtracting equation (3) from equation (2) is

$$p_1 - p_2 = -p^o_A X_{B_1} + p^o_B X_{B_1} + p^o_A X_{B_2} - p^o_B X_{B_2}, \tag{4}$$

which reduces to

$$p_1 - p_2 = (X_{B_1} - X_{B_2})\ (p^o_B - p^o_A) \tag{5}$$

The quantity $p_1 - p_2$ is the differential vapor pressure measured by the manometer, and $X_{B_1} - X_{B_2}$ is the difference in purity which was sought. For convenience these terms may be called Δp and ΔX_B respectively. Equation (5) then becomes

$$\Delta X_B = \frac{\Delta p}{p^o_B - p^o_A} \tag{6}$$

Washburn has derived an equation (unpublished report) which has a more general application since it takes account of Henry's law as well as that of Raoult. The form of the equation is the same as the one given above, but K_B, the Henry's-law constant for the impurity B, is substituted for p^o_B:

$$\Delta X_B = \frac{\Delta p}{K_B - p^o_A} \tag{7}$$

The difference in purity between two fractions is given by equation (6). If X_B in the middle cut may be assumed to be zero (which is frequently true), ΔX_B of the equation gives the amount of the impurity measured in the initial distillate (or in the final residue). If most of the impurity B is contained in the initial distillate (or final residue), ΔX_B will indicate an amount approaching that of the actual impurity. If the above conditions do not obtain, and any Δp is measured, ΔX_B gives an amount of impurity less than the actual amount present. Since, in addition to the above, the ratio of the volume of the initial distillate (or the final residue) to the total sample is known, it is sometimes possible to compute the amount of impurity present in the original sample.

It is apparent that the difference $p^o_B - p^o_A$ must be reasonably large if ΔX_B is small, and Δp is to be easily measurable. Thus if it is desired to detect 0.0001 mole fraction of impurity, $p^o_B - p^o_A$ should be at least 500 mm (preferably more) in order that Δp may be measurable. For this reason, the temperature at which Δp is measured is chosen accordingly. It is obvious that the method becomes insensitive without modification of the manometer to determine impurities whose normal boiling points are too close to that of the approximately pure substance.

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FLOW IN ROOF GUTTERS

By K. Hilding Beij

ABSTRACT

The design of roof gutters, heretofore, has been solely a matter of judgment based on experience. In order to provide a more rational method, an experimental study of the basic problem of roof gutters was undertaken. This problem may be stated as follows: What is the capacity of a straight open trough of uniform cross section, one end closed and the other end discharging freely, when the quantity of water flowing past a given cross section is directly proportional to the distance of the cross section from the closed end of the trough? Tests were made on rectangular and semicircular gutters of various lengths and widths, both level and sloping, and on one gutter of irregular cross section. Level gutters only are discussed in this paper.

Empirical formulas are given for determining capacity of level rectangular and semicircular gutters, and graphs for rapid solution are presented. An approximate method for gutters of irregular cross section, based on the tests of one such gutter, is also given.

Theoretical formulas for level gutters or channels of rectangular, triangular, trapezoidal, and semicircular cross sections are derived. The formulas for rectangular channels are compared with the results of the tests.

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I. INTRODUCTION

The investigation which forms the subject of this paper was one of the problems included in a research on copper roofing conducted jointly by the Copper and Brass Research Association and the Bureau of Standards.

The purpose of the investigation was to provide a more satisfactory basis for the design of roof gutters and leader connections than the arbitrary and widely variant rules now used. Because of limitations of time and facilities, the investigation was confined to the basic problem of roof gutters, which may be stated as follows: What is the capacity of a straight, open trough of uniform cross section, one end closed and the other end discharging freely, when the quantity of water flowing past a given cross section is directly proportional to the distance of the cross section from the closed end of the trough?

Because of the complex nature of the flow in sloping roof gutters, satisfactory formulas have not been developed from the experimental results. Accordingly, this paper deals only with level gutters.

II. APPARATUS

Figure 1 shows the manner in which gutters were mounted for test, the method of supplying water to the gutters, and the type of piezometer used. The pipe layouts for large and small flows are shown in

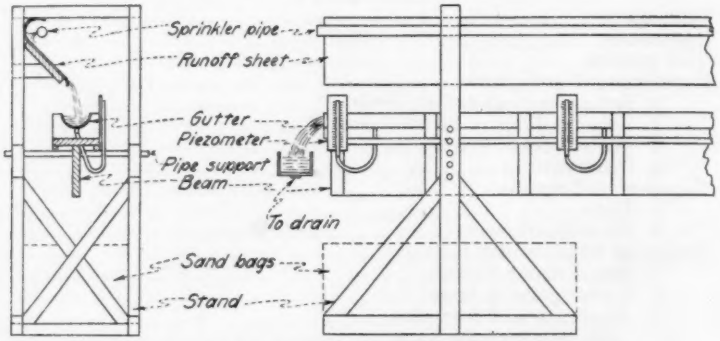


FIGURE 1.—*Sketch of apparatus for tests of roof gutters.*

figure 2. A 2-inch Hersey water meter, equipped with a 10 cubic-foot dial divided at 1 cubic-foot intervals and rated at the Bureau of Standards, was used.

III. TEST GUTTERS

A descriptive list of the level gutters which were tested is given in table 1. Note that some of the 6-inch gutters were tested with outlets instead of freely discharging from the end. In figure 3 are given drawings of the outlets used and sketches showing the position of outlets under the various test conditions. The form of cross section of the molded gutter, no. 27, in table 1, is shown in figure 4.

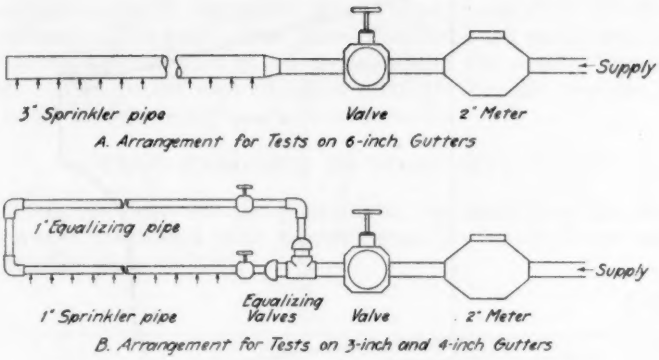
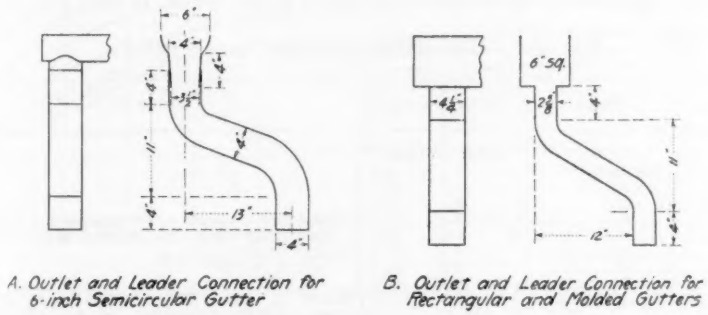


FIGURE 2.—*Diagram of piping for tests of roof gutters.*



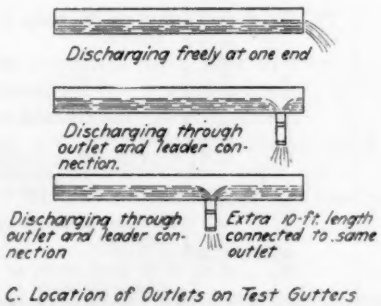

Discharging freely at one end
Discharging through outlet and leader connection.
Discharging through outlet and leader connection
Extra 10-ft length connected to same outlet
C. Location of Outlets on Test Gutters

FIGURE 3.—*Outlets and leader connections used in tests of roof gutters.*

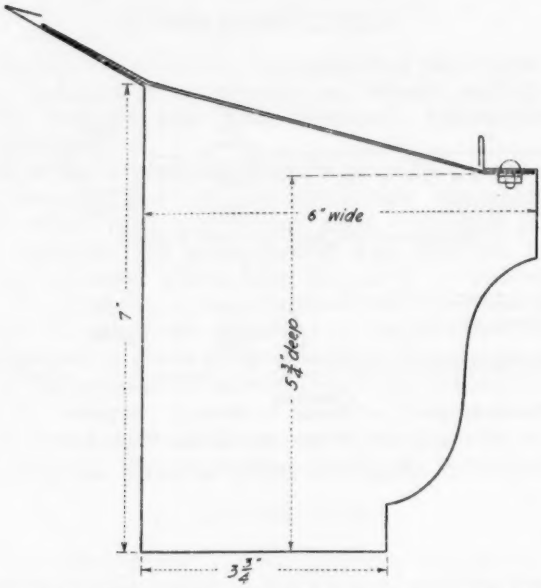


FIGURE 4.—*Cross section of molded gutter (no. 27 in table 1).*

TABLE 1.—*Descriptive list of level gutters tested.*

No.	Shape	Width	Length	Remarks
		Inches	*Feet*	
1	Semicircular	6	6.5	With 4-inch diameter outlet connected to goose-neck discharging freely. See *A* and *C* in figure 3.
2	do	6	11.5	
3	do	6	16.5	
4	do	6	21.5	
5	do	6	26.5	
6	do	6	31.5	
7	do	6	36.5	
8	do	6	41.5	
9	do	6	31.5	Outlet as above. Extra 10-foot length of gutter connected to same outlet. See *A* and *C* in figure 3.
10	do	6	6.5	With free discharge from end of gutter. See *C* in figure 3.
11	do	6	11.5	
12	do	6	16.5	
13	do	6	21.5	
14	do	6	26.5	
15	do	6	31.5	
16	do	6	36.5	
17	do	6	41.5	
18	do	6	41.5	
19	do	4	6.8	With free discharge from end of gutter. See *C* in figure 3.
20	do	4	16.5	
21	do	4	21.5	
22	Rectangular	6	31.6	With 4¼ inch by 2⅝ inch outlet lengthwise in gutter Extra 10-foot length of gutter connected to same outlet. See *B* and *C* in figure 3.
23	do	3	7.0	With free discharge from end of gutter. See *C* in figure 3.
24	do	3	12.0	
25	do	3	17.0	
26	do	3	22.0	
27	Molded	6	31.5	With same outlet as no. 22 above. Extra 10-foot length connected to same outlet. See *C* in figure 3. See figure 4 for shape of cross section.

IV. EXPERIMENTAL PROCEDURE

1. ADJUSTMENT OF GUTTER LEVELS

Final adjustments of the gutter levels were made with reference to a water surface. The gutter was partially filled with water and depths were measured at intervals of 30 inches along the center line with a point gage. The gutter was adjusted until the depths were as nearly uniform as possible.

2. ZERO READINGS OF PIEZOMETERS

The differences between the piezometer readings and the average depth of water measured with a point gage as before gave the zero readings for the piezometers.

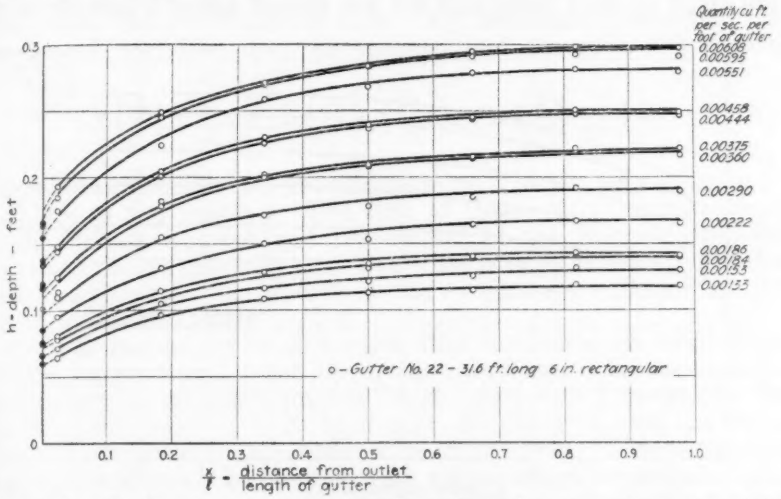


FIGURE 5.—*Depths of water in 6-inch rectangular gutter for various rates of flow. The solid black points represent computed values for the depth at the point of outflow.*

3. WATER MEASUREMENT

In general, the time required for a flow of 10 cubic feet as indicated by the meter was measured by a stop watch. For very low rates of flow the time for 5 cubic feet was measured. The rate of flow thus determined, corrected according to the meter calibration curve and divided by the length of the perforated pipe, gave the inflow per foot of gutter. The error in the corrected meter reading did not exceed one half of 1 percent.

4. OBSERVATIONS

A typical test run consisted of 15 observations on each piezometer as follows: The flow was adjusted to the lowest rate practicable and a few minutes allowed for it to become steady. Then all piezometers were read while the rate of flow was being measured. This set of readings was repeated, and the averages of the two sets constituted one observation.

V. EXPERIMENTAL RESULTS

1. DATA

The data are too voluminous for complete presentation. Therefore, only the data for one 6-inch rectangular and part of the data for two 6-inch semicircular gutters are given in figures 5 and 6.

2. FLOW DISTRIBUTION

The curves in figure 6 give an indication of the uniformity of flow from the sprinkler pipe. In obtaining these results a single long gutter was used, separated into two independent sections of equal length by a partition at the middle.[1] As shown by the graph, the results on the two gutters differed slightly. However, the differences were small in most cases and did not exceed about 5 percent in the

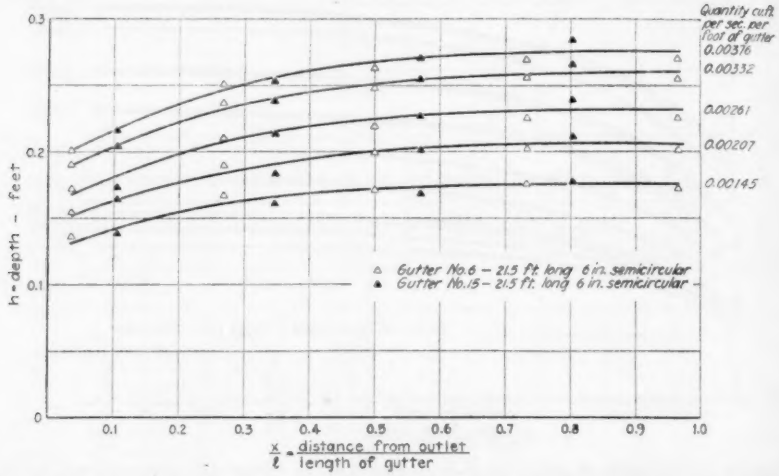


FIGURE 6.—*Depths of water in 6-inch semicircular gutters for various rates of flow.*

worst case. For simplicity, therefore, it was assumed that the discharge was uniformly distributed. This assumption implies that the average curves shown in figure 6 represent the results on both gutters.

VI. EMPIRICAL FORMULAS FOR CAPACITY

1. SEMICIRCULAR GUTTERS

The following notation will be used, and all quantities expressed in units of feet and seconds.

l = length of gutter.
b = width of gutter.
x = distance from outlet to any point on gutter.
h = depth of water.
q = inflow per foot of gutter per second.
Q = total inflow ($Q = ql$).
g = acceleration of gravity.

[1] This method of securing tests on two gutters simultaneously was adopted for nearly all of the experiments on level gutters.

The problem is to determine from the experimental data the depth of water h at any desired distance x from the outlet of a gutter in terms of the dimensions of the gutter, the physical properties of water, and the amount of inflow; and in particular, the depth at the upper end of the gutter, since this determined the capacity.

The physical properties of water which may be involved in the problem are

μ = viscosity,
ρ = density,
and τ = surface tension.

To take account of the roughness of the gutter surface, we can introduce a friction coefficient such as the dimensionless factor f.

Then h = function $(l, b, x, q, g, \mu, \rho, \tau, f)$, (1)

where the form of the function is to be determined so as to be in agreement with the experimental data. By dimensional analysis,[2] the number of variables may be reduced and equation (1) becomes

$$\left(\frac{h}{l}\right) = F\left[\left(\frac{q^2}{l^3 g}\right), \left(\frac{q\rho}{\mu}\right), \left(\frac{l\tau}{\rho q^2}\right), (f), \left(\frac{b}{l}\right), \left(\frac{x}{l}\right)\right], \tag{2}$$

where F is a function (as yet undetermined) of the six dimensionless variables in the bracket. The first of these variables corresponds to the Froude number and the second to the Reynolds number. The third has no generally used name but may be called the "surface tension number." The fourth is the roughness coefficient and the others are shape factors.

We will assume for simplification that the Reynolds number, the surface tension number and the friction coefficient may be neglected in deriving the general equation for the gutters. This implies that the Reynolds number is so high that the energy losses are almost wholly determined by the turbulance of the flow. This assumption is arbitrary and can be justified only by the results obtained. Also, even if we find the assumption to be legitimate within the range of the experiments, it must be borne in mind that if the range is extended (to larger or smaller gutters, to different liquids, or to gutters with different roughness) the results may not be applicable. With this assumption equation (2) simplifies to

$$\left(\frac{h}{l}\right) = F\left[\left(\frac{q^2}{l^3 g}\right), \left(\frac{b}{l}\right), \left(\frac{x}{l}\right)\right]. \tag{3}$$

From the data it was found that equation (3) could be replaced with a close approximation by

$$\left(\frac{h}{l}\right) = \left(\frac{q^2}{l^3 g}\right)^{\frac{1}{3}} \left(\frac{b}{l}\right)^{-\frac{1}{3}} F_1\left(\frac{x}{l}\right), \tag{4}$$

where F_1 represents an undetermined function.

Equation (4) may be rewritten

$$h\left(\frac{gb}{q^2 l^2}\right)^{\frac{1}{3}} = F_1\left(\frac{x}{l}\right). \tag{5}$$

[2] E. Buckingham, Model experiments and the forms of empirical equations. Trans. A.S.C.E., vol. 37, 1915.

Values of the left-hand member of equation (5) computed from the data are plotted in figure 7 as a function of $\left(\frac{x}{l}\right)$. Each point represents the result of the 15 observations at one piezometer on one gutter.

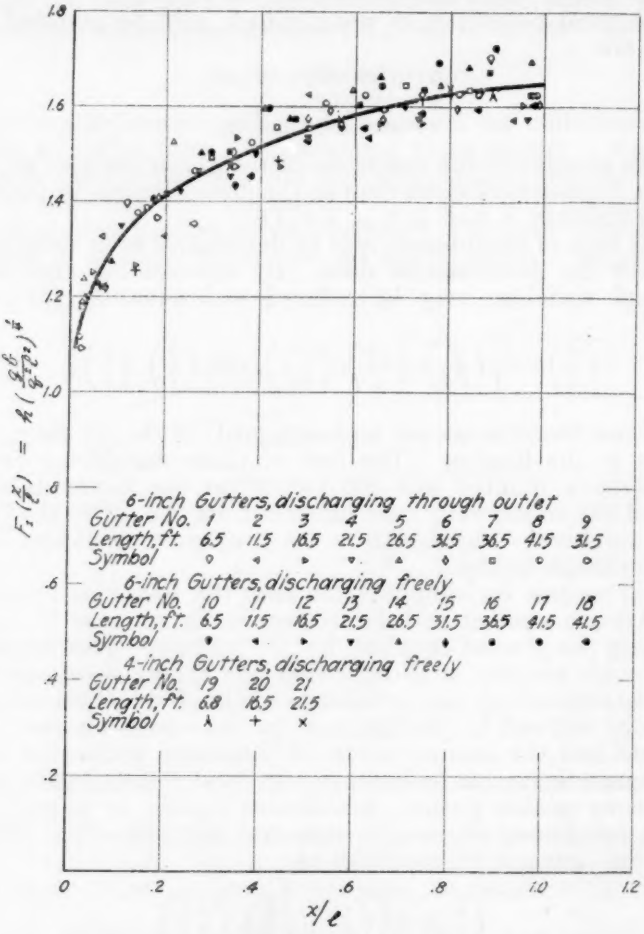


FIGURE 7.—*Values of* $F_1\left(\frac{x}{l}\right)=h\left(\frac{gb}{q^2l^2}\right)^{\frac{1}{3}}$ *for semicircular gutters. The approximation curve is given by the equation* $F_1\left(\frac{x}{l}\right)=1.65\left(\frac{x}{l}\right)^{1/6}$.

The curve drawn in figure 7, which is a graph of the equation,

$$F_1=1.65\left(\frac{x}{l}\right)^{1/6}, \tag{6}$$

is adopted as an approximate representation of the plotted points. Substituting this value of F_1 in equation (5) and solving for h, there results

$$h=1.65\left(\frac{q^2l^2}{gb}\right)^{\frac{1}{3}}\left(\frac{x}{l}\right)^{1/6}, \tag{7}$$

which is the complete formula for flow in level semicircular roof gutters.

To obtain a formula for capacity, it should be noted that the maximum depth occurs at the upper or closed end. If the depth of water here is equated to the total depth of the gutter, then substituting in (8) the following values;

$$h=\frac{b}{2},\ x=l,\ Q=ql,\ g=32.2,$$

there is obtained finally

$$Q=0.52b^{\frac{5}{2}}, \tag{8}$$

which gives the capacity in cubic feet per second of a semicircular level gutter in terms of its width in feet. Inverting equation (8), there results

$$b=1.3Q^{\frac{2}{5}}, \tag{8a}$$

which gives the width in feet of a semicircular level gutter required for a known flow.

2. RECTANGULAR GUTTERS

Similarly, there was found for rectangular gutters the equation

$$\left(\frac{h}{l}\right)=\left(\frac{q^2}{l^3g}\right)^{\frac{1}{5}}\left(\frac{b}{l}\right)^{-\frac{3}{5}}F_1\left(\frac{x}{l}\right), \tag{9}$$

which may be written

$$h\left(\frac{g^5b^{12}}{q^{10}l^{13}}\right)^{\frac{1}{15}}=F_1\left(\frac{x}{l}\right). \tag{10}$$

Values of the left-hand member of equation (10) computed from the data are plotted in figure 8. The curve, which is a graph of the equation

$$F_1=0.823\left(\frac{x}{l}\right)^{\frac{1}{2}}, \tag{11}$$

is adopted as an approximate representation of the plotted points.

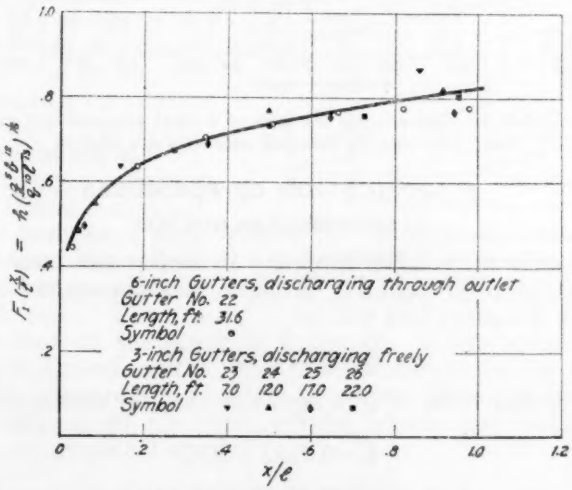


FIGURE 8.—*Values of* $F_1\left(\frac{x}{l}\right)=h\left(\frac{g^5b^{12}}{q^{10}l^{13}}\right)^{\frac{1}{15}}$ *for rectangular gutters. The approximation curve is given by the equation* $F_1\left(\frac{x}{l}\right)=0.823\left(\frac{x}{l}\right)^{\frac{1}{2}}$.

Substituting this value of F_1 in equation (11) and solving for h, there results

$$h = 0.823 \left(\frac{q^{10} l^{13}}{g^5 b^{12}}\right)^{\frac{1}{16}} \left(\frac{x}{l}\right)^{\frac{1}{8}}, \tag{12}$$

which is the complete formula for flow in level rectangular roof gutters.

It is convenient to deal with the ratio of the depth of a rectangular gutter to its width, as follows:

$$m = \frac{\text{depth of gutter}}{\text{width of gutter}}$$

Then for a gutter carrying its maximum flow, we have as before:

$$h = mb,\ x = l,\ Q = ql,\ g = 32.2,$$

so that equation (12) reduces to

$$Q = 7.75 m^{\frac{5}{8}} \left(\frac{b}{l}\right)^{\frac{1}{16}} b^{\frac{5}{2}}, \tag{13}$$

and

$$b = 0.483 m^{-\frac{1}{3}} l^{\frac{1}{3}} Q^{\frac{2}{3}}. \tag{13a}$$

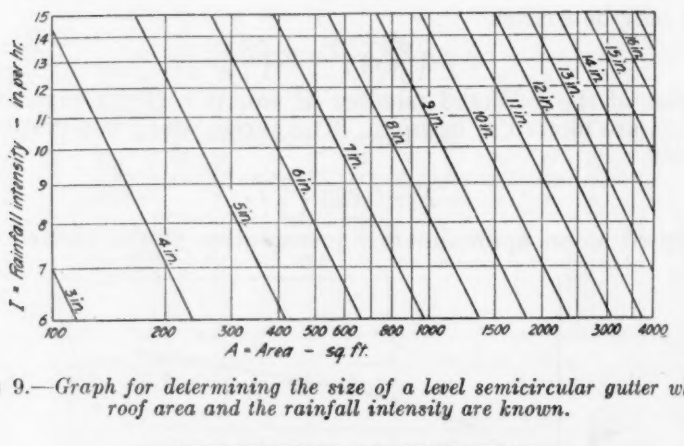


FIGURE 9.—*Graph for determining the size of a level semicircular gutter when the roof area and the rainfall intensity are known.*

3. APPLICATION OF FORMULAS

(a) SEMICIRCULAR GUTTERS

If the maximum rainfall intensity in inches per hour be denoted by I, then the total quantity in cubic feet per second falling on a roof of area A square feet will be

$$Q = 2.31 \times 10^{-5} IA. \tag{14}$$

Substituting this value of Q in equation (8a) for semicircular gutters, the result is

$$b = 0.0182\,(IA)^{\frac{1}{2}}, \tag{15}$$

which gives the width in feet of gutter required when the rainfall intensity and the roof area are known. The formula is conveniently solved by means of a graph such as that in figure 9.

In the graph, the gutter widths are expressed in inches as this is the customary unit. By roof area, the area of the horizontal projection of the roof is understood; that is, roof areas should be computed from the roof plans. If the roof is not rectangular, the dimensions of the rectangle enclosing the plan may be taken instead of the actual roof dimensions, provided the inflow is nearly uniformly distributed along the gutter.

(b) RECTANGULAR GUTTERS

By substitution of equation (14) in equation (13a) there is obtained for rectangular gutters the formula

$$b = 0.0106 m^{-\frac{1}{3}} l^{\frac{1}{3}} (IA)^{\frac{4}{9}}, \tag{16}$$

which can be readily solved with the aid of the graphs in figures 10 and 11.

(c) GUTTERS OF IRREGULAR CROSS SECTION

The required sizes of level gutters of other than semicircular or rectangular shapes can be determined approximately by finding the semicircle or rectangle of the same area which most closely fits the irregular cross section as in figure 12.

This method of approximation for gutters of irregular cross section was checked by data obtained on a molded copper gutter. For each depth of flow, the width of a rectangle of the same area as the filled part of the cross section was determined. The extreme cases are shown by (c) and (d) in figure 12. From these dimensions and the length of the gutter, the corresponding computed values of the quantity $(IA) = Q$ were determined by means of the graphs in figures 10 and 11. These computed values were compared with observed values determined from the known quantity of flow in each case. The results are plotted on the graph in figure 13. If the values found by both methods agreed exactly, the points represented by the circles would fall on the straight line. It is evident that the discrepancies are very small except for three points, which may very likely be affected by experimental error.

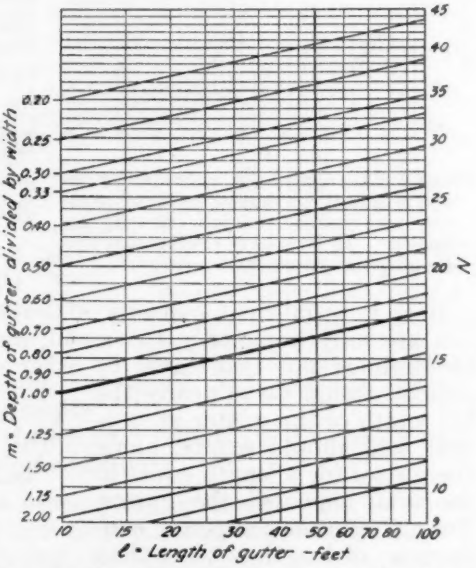


FIGURE 10.—*Graph for determining the size of a level rectangular gutter when the roof area and the rainfall intensity are known. To be used in conjunction with the graph in figure 11.*

(d) FACTOR OF SAFETY

The annoyance and damage resulting from occasional overflows of over-loaded gutters depend upon the character of the building under consideration, and their importance is a matter of judgment which

must be left to the architect or designing engineer. The duration and intensity of heavy rains and the frequency with which they may be expected to occur may be ascertained for any given locality by application to the nearest station of the United States Weather Bureau or the local forecaster. Then the intensity to be used in design may be chosen according to circumstances. The intensity should be picked in each case high enough so that the gutter dimensions determined from the graphs can be used directly without multiplying by some arbitrary "factor of safety."

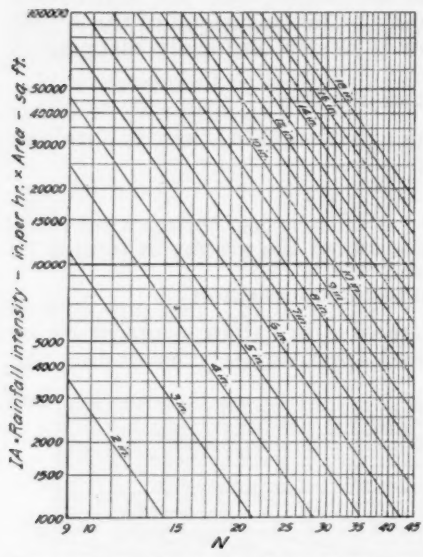


FIGURE 11.—*Graph for determining the size of a level rectangular gutter when the roof area and the rainfall intensity are known. To be used in conjunction with the graph in figure 10.*

(e) SLOPING GUTTERS

Sloping gutters carry much more water than level gutters of the same size. The graphs for level gutters may be used, however, to check dimensions chosen for sloping gutters. If the selected dimensions are greater than those given by the charts, it is obvious that the gutter will be unnecessarily large.

(f) LEADER CONNECTIONS

The usual cause of overflowing gutters is insufficient capacity of leader connections. Gutter outlets are very commonly too small, and may be further obstructed by strainers and also leaves or other debris. It is suggested that outlets should be as nearly the full width of the gutter as possible and should extend along the gutter for a length equal to the total depth of the gutter. From the outlet a tapering connection, of length not less than its maximum width, should lead to the conductor. If two gutters empty into the same leader, then the outlet should be half again as long as for a single gutter. For structural or architectural reasons, such outlets may be too large, in which case more leaders should be provided and the gutter dimensions recomputed. These suggestions are based on the limited observations furnished by the tests, and therefore are subject to revision in the light of more complete information.

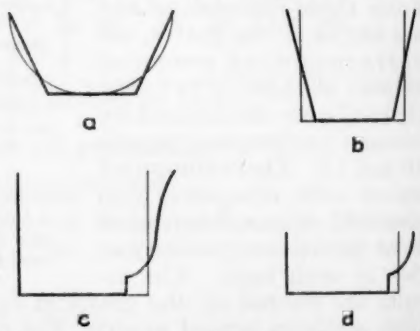


FIGURE 12.—*Approximation of gutters of trapezoidal or irregular cross section by semicircles and rectangles.*

When two outlets are provided at the ends of a single gutter, one half the gutter length and one half the roof area should be used in computing the gutter dimensions.

VII. THEORETICAL ANALYSIS

1. GENERAL EQUATION OF FLOW

The empirical formulas which have been derived are adequate for determining the dimensions of roof gutters, because in this particular case only approximate results are needed. They should not, however, be applied to channels of dimensions widely different from those of the gutters tested, for in addition to the limitation introduced by the assumption of a high Reynolds number they are also only arbitrary functions of the remaining variables which have been worked out to fit the experimental results. Beyond the limits of the experiments these functions may still be valid, but it is also possible that they may diverge more and more from fact even within the limits of high Reynolds numbers and finally lead to results grossly in error. Furthermore, the formulas in themselves do not lead to any general results of interest. For these reasons and because the procedure used in deriving the formulas was inadequate for sloping gutters, a more detailed study was started. This study is not yet completed, but the results so far obtained are given here.

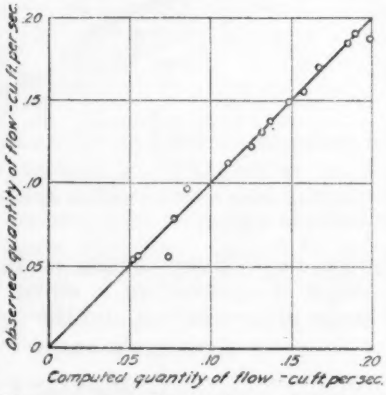


FIGURE 13.—*Comparison of observed quantities of flow with flows computed by approximation method for gutters of irregular cross sections.*

For convenience, the origin of coordinates is taken at the upper end of the gutter instead of the outlet. Otherwise the same notation will be used, with the following additions:

M = mass per unit time passing any cross section.
q = volume inflow per unit time per unit length of gutter.
w = specific weight of water.
v = average velocity at any cross section.
a = area of water cross section at any point.
i = slope of gutter bottom.
J = slope of water surface.
f = frictional force per unit area of boundary of stream.

The following assumptions will be made:

1. As assumed in deriving the empirical equations, the effects of surface tension and viscosity may be neglected. This implies that the Reynolds number is so high that the energy losses are almost wholly determined by the turbulence of the flow.

2. The mean velocity of the mass M (or quantity qx) at any cross section is equal to the average velocity in the cross section [3] and is given by the volume of flow divided by the area of the cross section $v=qx/a$.

3. Vertical components of velocity are negligible; since the slope J of the water surface and the slope i of the gutter are both small.

4. The water flowing into the gutter enters with a zero component of momentum in the direction of flow. This is equivalent to saying that the kinetic energy of the inflowing water is dissipated (as heat in eddies, etc.) and has no effect on the motion in the gutter.

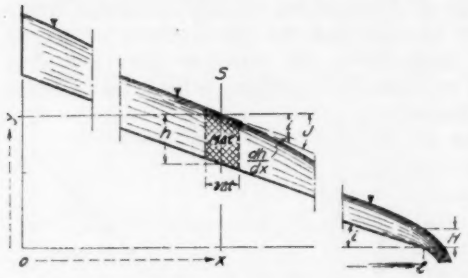


FIGURE 14.—*Diagram of surface curve in roof gutter showing notation used in deriving theoretical formulas.*

Consider the mass, $M\cdot\Delta t$, of water passing a cross section, S, in time Δt; see figure 14. The length of this mass of water will be $v\cdot\Delta t$. Then, since the time rate of change of momentum is equal to the external forces acting, we have for the equation of flow

$$\frac{d}{dt}(M\cdot\Delta t\cdot v)=G-F, \qquad (17)$$

where G and F represent the gravitational and frictional forces, respectively, acting on the mass $M\cdot\Delta t$. Also the time rate of change of momentum is equal to the product of the space rate of change of momentum and the velocty, so that equation (17) becomes

$$\frac{d}{dt}(M\cdot\Delta t\cdot v)=v\frac{d}{dx}(M\cdot\Delta t\cdot v)=G-F. \qquad (18)$$

The free surface of the mass $M\cdot\Delta t$. which is displaced a horizontal distance Δx, through the section x, drops by an amount Δy so that its potential energy decreases by $M\Delta t\cdot g\cdot\Delta y$. This decrease, divided by Δx, gives the x-component of the effective force G due to gravity, so that

$$G=M\Delta t\cdot g\frac{dy}{dx}=M\Delta t\cdot gJ$$

Also,

$$J=i-\frac{dh}{dx},$$

so that, finally,

$$G=M\cdot\Delta t\cdot g\left(i-\frac{dh}{dx}\right) \qquad (19)$$

[3] This is strictly true only when the velocity is constant over the entire cross section. Assuming uni width of stream, we have mean velocity $=\bar{v}=\int_0^h v^2dy\Big/\int_0^h vdy$, where v is some function of y (the height above the stream bottom); and

$$\text{average velocity}=v_a=\frac{1}{h}\int_0^h vdy.$$

It is evident that $\bar{v}$ is not equal to v_a unless v is a constant. Also $\bar{v}$ cannot be calculated unless the velocity distribution over the cross section is known.

The frictional force, F, is assumed to depend on the velocity and the area of contact between the water and the sides and bottom of the gutter, as follows:

$$F = f\frac{v^2}{2g}pv\cdot\Delta t, \tag{20}$$

where $f\frac{v^2}{2g}$ is the frictional force per unit area of contact; and p is the wetted perimeter at the section S, so that $pv\cdot\Delta t$ is the area of contact.

By the substitution of (19) and (20) in (18), we have

$$v\frac{d}{dx}(Mv) = Mg\left(i-\frac{dh}{dx}\right)-f\frac{v^2}{2g}pv, \tag{21}$$

Substituting

$$M=\frac{qwx}{g} \text{ and } v=\frac{qx}{a},$$

we obtain finally

$$\frac{q^2}{g}\frac{d}{dx}\left(\frac{x^2}{a}\right)=a\left(i-\frac{dh}{dx}\right)-\frac{fq^2}{2gw}\cdot\frac{px^2}{a^2}. \tag{22}$$

Equation (22) is the general equation for gutters or channels in which the quantity flowing at any section is proportional to the distance from the upper end. Note that both a and p are functions of the depth and such constants as are required to define the shape of the gutter. The equation is it stands, therefore, cannot be integrated. Solutions have been obtained, however, for certain special cases which are given below.

2. LEVEL GUTTERS WITHOUT FRICTION

If we assume that the frictional forces are sufficiently small so that their effects can be neglected and also that the gutters are horizontal, then equation (22) reduces to a much simpler form as follows.[4]

$$\frac{q^2}{g}\frac{d}{dx}\left(\frac{x^2}{a}\right)=-a\frac{dh}{dx}. \tag{23}$$

Evidently, both members of the equation are perfect differentials (a being a function of h only) and the solution is, accordingly,

$$\frac{q^2x^2}{ga}=-\int_0^x a\frac{dh}{dx}dx=-\int_{h_o}^{h}adh, \tag{24}$$

where h_o is the depth at $x=0$ (closed end of trough)

Let H be the depth at the outlet end of the trough. (This depth is known from other considerations, as will be shown later.) When $x=l$, $h=H$, and we can write

$$\frac{q^2l^2}{gA}=-\int_{h_o}^{H}adh, \tag{25}$$

[4] This result expressed in a slightly different form has previously been obtained by Julian Hinds. See "Side Channel Spillways", Trans. A.S.C.E., vol. 89, p. 881, 1926.

where A is the cross-sectional area corresponding to H. Subtracting (25) from (24) and simplifying

$$-\frac{ga}{q^2l^2}\int_h^H adh-\frac{a}{A}+\frac{x^2}{l^2}=0, \tag{26}$$

which is the general equation, friction being neglected, for level channels in which the quantity flowing at any point is proportional to the distance from one (closed) end.

3. EVALUATION OF H

So far, H has been defined only as the depth at the point of outflow of the gutter. In order to make use of equation (26) it is necessary to find a method of evaluating this depth. If we assume that the flow always adjusts itself so as to make the total energy of the stream at the outflow section a minimum, then this section is a *critical* section and the depth H can be computed.[5] The experimental justification for this assumption is presented in part in figure 5.

Critical depths, computed for the outlet section for each quantity of flow, are plotted as solid circles on the ordinate axis. The extensions of the surface curves by the dotted lines pass quite near the corresponding critical depths, indicating that the assumption is valid within the limits of experimental errors. Similar results were obtained for all of the gutters tested. A very close agreement cannot be expected, since the computed values are based on assumption that the curvature of the water surface is negligible, and this assumption is obviously not fulfilled in this particular case.

To evaluate the critical depth H, we note that the total energy of flow, E, at a cross section is the sum of the potential and kinetic energies, so that

$$E=MgH+\frac{1}{2}MV^2,$$

computed with reference to the bottom or invert of the channel. The condition for a minimum is

$$\frac{dE}{dH}=Mg+MV\frac{dV}{dH}=0,$$

or

$$g+V\frac{dV}{dH}=0. \tag{27}$$

At the point of outflow,

$$V=\frac{ql}{A},$$

and substitution of this value in (27) gives

$$g+\frac{ql}{A}\cdot\frac{d}{dH}\left(\frac{ql}{A}\right)=0,$$

whence,

$$\frac{q^2l^2}{g}=\frac{A^3}{\left(\frac{dA}{dH}\right)}.$$

[5] Handbook of Hydraulics, by H. W. King, McGraw-Hill Book Co., Inc., 1929. Hydraulics of Open Channels, by B. A. Bakhmeteff, McGraw-Hill Book Co., Inc., 1932.

If we denote the width of the water surface by B,

$$\frac{dA}{dH}=B,$$

so that

$$\frac{q^2l^2}{g}=\frac{A^3}{B}, \tag{28}$$

a general equation, applying to any form of cross-section.

In order to proceed further it is necessary to specify the shape of the gutter. A number of the more common shapes are treated below.

(a) RECTANGULAR

For a rectangular gutter of width b, we have

$$A=bH, \tag{29}$$

$$B=b, \tag{29a}$$

and hence from (28)

$$\frac{q^2l^2}{g}=\frac{b^3H^3}{b}, \tag{29b}$$

or

$$\mathrm{H}=\sqrt[3]{\frac{q^2l^2}{gb^2}}, \tag{29c}$$

(b) TRIANGULAR

The gutter consists of two sides, with any slopes equal or unequal, meeting at any angle so that the vertex of the cross section is at the lowest point. Then the width of the water surface, B, is proportional to the depth, so that

$$A=\frac{1}{2}kH^2, \tag{30}$$

and

$$B=kH, \tag{30a}$$

where k is a constant determined by the slopes of the sides. Hence from (28)

$$\frac{q^2l^2}{g}=\frac{1}{8}\frac{k^3H^6}{kH}=\frac{1}{8}k^2H^5, \tag{30b}$$

or

$$H=\sqrt[5]{8\frac{q^2l^2}{gk^2}}. \tag{30c}$$

(c) TRAPEZOIDAL

The cross section is in the form of a trapezoid with one level side forming the bottom and two sides sloping upward, the slopes not necessarily equal.

Then

$$A=sH+\frac{1}{2}kH^2=H\left(s+\frac{1}{2}kH\right), \tag{31}$$

$$B=s+kH, \tag{31a}$$

where s is the constant width of the bottom of the gutter, and k is a constant depending upon the slopes of the sides. By substitution in (28)

$$\frac{q^2l^2}{g}=H^3\frac{\left(s+\frac{1}{2}kH\right)^3}{s+kH}, \tag{31b}$$

from which the value of H may be computed for any specified case.

(d) SEMICIRCULAR

Let r be the radius of the cross section. Then

$$A=r^2\cos^{-1}\left(\frac{r-H}{r}\right)-(r-H)\ (2rH-H^2)^{\frac{1}{2}}, \tag{32}$$

$$B=2(2rH-H^2)^{\frac{1}{2}}. \tag{32a}$$

Substituting in (28)

$$\frac{q^2l^2}{g}=\frac{\left[r^2\cos^{-1}\left(\frac{r-H}{r}\right)-(r-H)\ (2rH-H^2)^{\frac{1}{2}}\right]^3}{s(2rH-H^2)^{\frac{1}{2}}} \tag{32b}$$

4. EQUATIONS FOR PARTICULAR CASES

We now proceed to determine the form of equation (26) for the various particular cases.

(a) RECTANGULAR

From equation (26) by substitution of the results given by (29) to (29c), inclusive, we obtain

$$\left(\frac{h}{H}\right)^3-3\left(\frac{h}{H}\right)+2\left(\frac{x}{l}\right)^3=0. \tag{33}$$

The maximum depth occurs at the upper end of the gutter where $x=0$, and is given by

$$h_0=\sqrt{3}H. \tag{33a}$$

If the ratio of the depth to the width of the gutter is m, then the capacity Q is

$$Q=2.5m^{\frac{1}{2}}b^{\frac{5}{2}}, \tag{33b}$$

where Q is in cubic feet per second and b is in feet.

(b) TRIANGULAR

From (26) and (30) to (30c), inclusive, we have

$$2\left(\frac{h}{H}\right)^5-5\left(\frac{h}{H}\right)^2+3\left(\frac{x}{l}\right)^2=0. \tag{34}$$

The maximum depth, at $x=0$, is given by

$$h_0=\sqrt[3]{\frac{5}{2}}H, \tag{34a}$$

and the capacity Q by

$$Q=\frac{0.935}{k^{3/4}}b^{5/2}, \tag{34b}$$

where Q is in cubic feet per second, b is in feet, and k is the ratio of the top width b to the vertical depth of the channel.

(c) TRAPEZOIDAL

From equation (26) and equations (31) to (31b), inclusive, there results

$$\frac{h(s+kH)\left(s+\frac{1}{2}kh\right)}{H^3\left(s+\frac{1}{2}kH\right)^3}\left[\frac{h^2}{2}\left(s+\frac{1}{3}kh\right)-\frac{H^2}{2}\left(s+\frac{1}{3}kh\right)\right]-\frac{h\left(s+\frac{1}{2}kh\right)}{H\left(s+\frac{1}{2}kH\right)}+\left(\frac{x}{l}\right)^2=0, \tag{35}$$

which reduces to equation (33) if we put $s=b$ and $k=0$, or to equation (34) if we put $s=0$.

The maximum depth h_o occurs when $x=0$ and is given by the equation

$$h_o^2\left(s+\frac{1}{3}kh_o\right)-\frac{H^2}{s+kH}\left(s+\frac{1}{3}kH\right)(s+kH)+2\left(s+\frac{1}{2}kH\right)^2=0, \tag{35a}$$

and the capacity by eliminating H from equations (31b) and (35a) and solving for Q.

(d) SEMICIRCULAR

From equation (26) and equations (32) to (32b), inclusive, the equation for semicircular channels becomes

$$\frac{aB}{A^3}\left[3\{A(r-H)-a(r-h)\}+2\left\{\left(\frac{b}{2}\right)^3-\left(\frac{B}{2}\right)^3\right\}\right]-3\frac{a}{A}+3\left(\frac{x}{l}\right)^2=0, \tag{36}$$

and for the maximum depth,

$$\frac{B}{A^2}\left[3\{A(r-H)-a_o(r-h_o)\}+2\left\{\left(\frac{b_o}{2}\right)^3-\left(\frac{B}{2}\right)^3\right\}\right]-3=0. \tag{36a}$$

If the channel is filled, $h_o=r$, $b_o=2r$ and $a_o=\frac{\pi r^2}{2}$;

so that

$$\frac{B}{A^2}\left[3A(r-H)+2\left\{r^3-\left(\frac{B}{2}\right)^3\right\}\right]-3=0, \tag{36b}$$

and combining this result with (32b), the value of Q may be computed.

5. COMPARISON OF THEORETICAL RESULTS WITH EXPERIMENTAL DATA

In order to illustrate the degree of concordance between the theoretical formulas and the results of the experiments, the measured depths at the upper ends of the rectangular gutters are plotted in figure 15 against the corresponding depths computed by means of

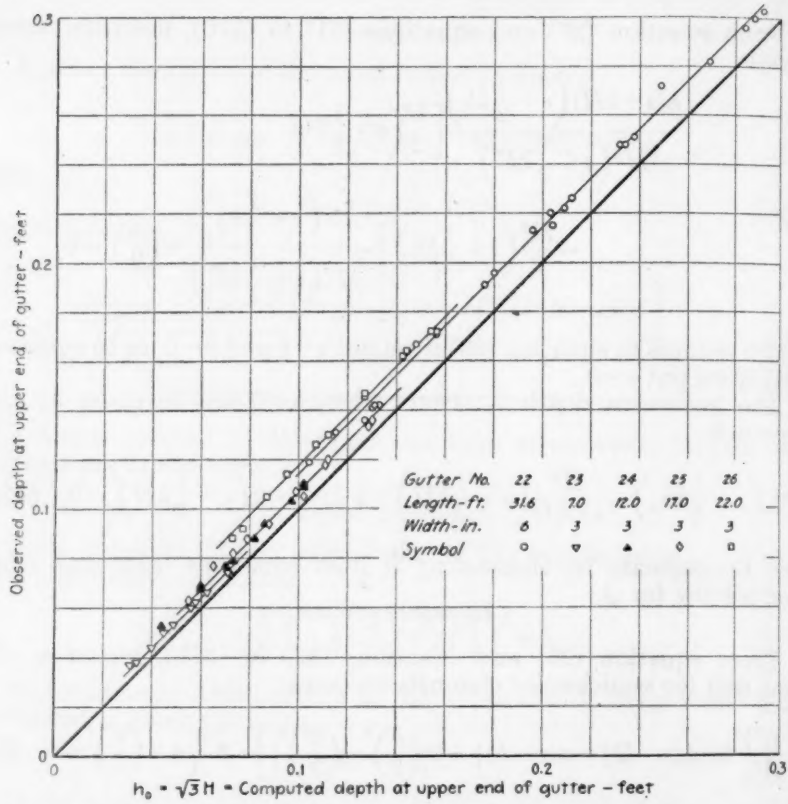


FIGURE 15.—*Comparison of observed depths with depths computed from theoretical equation (33a) for 3-inch and 6-inch rectangular gutters.*

equation (33a).

All of the observed depths are greater than the computed depths, since the resisting forces, such as friction, have been neglected in the derivation of the equation (33a).

For each gutter the difference between computed and observed depths is constant, or in other words, it is independent of the quantity flowing. The relative or percentage difference is, therefore, inversely proportional to the quantity flowing.

The results indicate that the differences between computed and actual depths for rectangular gutters depend on the gutter dimensions. The difference increases with increasing length and decreases with increasing width of gutter.

Further details will be left for future publication.

VIII. SUMMARY

1. Empirical formulas for the capacity of level semicircular and rectangular roof gutters have been deduced from the results of tests. Graphs for simplifying the solutions of the formulas are presented.

2. An approximate method for determining the capacity of level roof gutters of irregular cross section is suggested. The method has been checked by tests on one gutter.

3. Theoretical formulas, derived after certain simplifying assumptions, have been found for level rectangular, semicircular, triangular, and trapezoidal channels where the quantity flowing is proportional to the distance from one end of the channel. The theoretical results are compared briefly with the experimental data in the case of the rectangular channels.

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OLIVINE AS A REFRACTORY

By R. A. Heindl and W. L. Pendergast

ABSTRACT

Olivines representing three different deposits in North Carolina and one each in California, British Columbia, and Russia were tested to determine the possibilities of the material as a refractory. The chemical analyses were made on the raw materials, and linear thermal expansions, specific gravities, pyrometric cone equivalents, and petrographic analyses on both the raw and heated materials. The results show that olivine from North Carolina apparently has the necessary properties demanded of a high-grade special refractory and that it might be used in industrial processes where possible contamination by iron is of no consideration.

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I. INTRODUCTION

Olivine is a greenish, transparent to translucent mineral, usually occurring in granular aggregates or as small disseminated, glassy grains.[1] It is a silicate of iron and magnesium, 2 (Mg, Fe) $O.SiO_2$, and as found in nature is a solid solution of forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4).

Large quantities of this material are available in North Carolina and some speculation has arisen relative to its suitability as a special refractory. Since olivine is quite rich in magnesium, and if it should prove to be basic or semibasic in character, its use in certain metallurgical operations where magnesite is employed at present may be advantageous. This applies especially to its use in industries along the eastern seaboard, since magnesite must be shipped from either the West Coast or imported. Very little information is available relative to the properties of this material; consequently the desirability and necessity of additional information led to a short study of those properties which might aid in its classification.

[1] Raymond B. Ladoo, Nonmetallic Minerals, p. 417 (1925); also Winchell, Elements of Optical Mineralogy, pt. II, p. 166.

II. MATERIALS

Small samples of five olivines were secured from the National Museum and a sixth from the United States Bureau of Mines. The laboratory key letters and the approximate source of the material as furnished by the Museum are given in table 1. A sample of calcined magnesite secured from a manufacturer of refractory bricks was included for comparative purposes.

III. METHODS OF TESTING AND RESULTS

1. CHEMICAL ANALYSES

The chemical compositions of the several olivines are given in table 1. It may be noted that the content of magnesium oxide ranges from about 39 to 49 percent and is approximately one half that found in commercial magnesite brick. The lime content of the North Carolina materials is very small. The iron content of sample "F"[2] and the lime content of sample "D" is very high in comparison with that found in the remainder of the samples. The range in silica

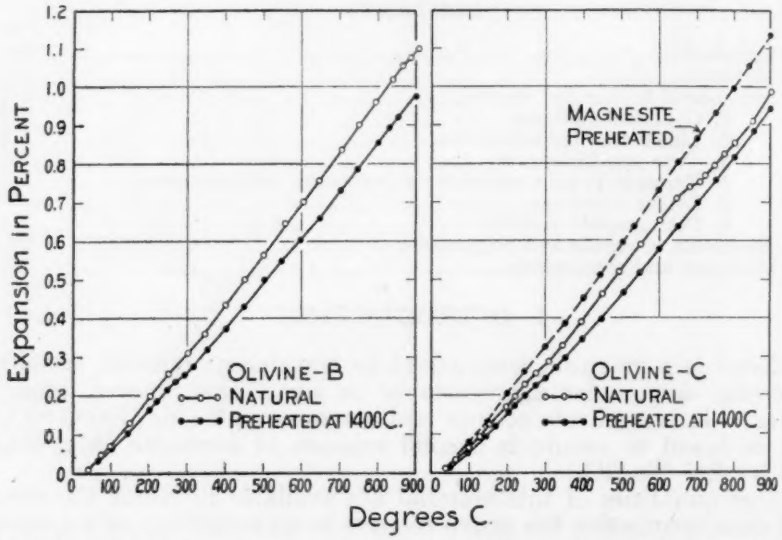

FIGURE 1.—*Linear thermal expansion of (1) untreated or raw olivine, (2) olivine after having been heated at 1,400 C, (3) calcined magnesite after heating at 1,400 C.*

content (40 to 45 percent) is rather narrow, approximating 5 percent from the lowest to the highest values.

2. LINEAR THERMAL EXPANSION

The linear thermal expansions of the olivines were measured from room temperature to 900 C with the interferometer.[3] The furnace was heated at an average rate of approximately 4 C per minute.

[2] This material is also known as "Glinkite." A System of Mineralogy, by E. S. Dana, p. 453 (1911 edition).

[3] C. G. Peters and C. H. Cragoe, B.S. Scientific Paper No. 393, and G. E. Merritt, B.S. Research Paper No. 515.

TABLE 1.—*Some physical and chemical properties of olivine*

Laboratory key letter	National Museum specimen number	Source of material	Chemical composition [1]								Linear thermal expansion				True specific gravity		P.C.E. (Softening point) [4]				Linear burned shrinkage (1,400 C for 5 hours)
			Ignition loss	SiO_2	Al_2O_3	FeO [2]	TiO_2	CaO	MgO	Fe_2O_3	Total 20 to 900 C		Average coefficient 20 to 900 C				Natural		Heated [3]		
											Natural	Heated [3]	Natural	Heated [3]	Natural	Heated [3]	Cone	°C	Cone	°C	
			Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	$\times 10^{-6}$	$\times 10^{-6}$							*Percent*
A	48,026	Jackson County, N.C.	1.11	40.46	0.25	9.05	1.32	0.05	47.81			0.949		10.8	3.206	3.340	35+	Over 1,785	35+	Over 1,785	2.1
B	96,252	Balsam Gap, N.C.	.53	41.83	.87	6.93	.63	.05	48.81		1.082	.976	12.4	11.1	3.255	3.342	35+		35+		3.3
C		Franklin, N.C.	.86	40.63	.10	10.28	1.10	.01	46.82		.987	.942	11.3	10.8	3.285	3.371	35+		35+		3.3
D	94,430	Ludlow, Calif.	.29	45.28	2.74	7.68	1.62	3.04	39.18			.936		10.6	3.334	3.301	11 to 16	1,325 to 1,465	26	1,595	13.5
E	96,356	Timothy Mt., B. C.	.33	44.87	2.20	7.93	.81	.70	42.99			.992		11.3	3.332	3.294	30	1,650	27 to 28	1,610	9.9
F	16,257	Urals, Russia	.60	39.78	.00	15.67	1.82	.01	42.36		1.025	1.032	11.7	11.8	3.420	3.434	32 to 33	1,723	32	1,700	3.3
Magnesite (calcined)			.57	1.95	.67			1.65	93.05	2.04		1.137		13.0		3.50					1.2

[1] Olivines analyzed by J. F. Klekotka, of the Bureau staff. The analysis of the calcined magnesite was furnished by the company from which the material was obtained.
[2] All the iron in the sample is reported as ferrous oxide and no attempt was made to determine the amount of iron that might have been present as ferric oxide.
[3] Materials were preheated at 1,400 C for five hours before tests were made.
[4] End points were measured with pyrometric cones. Temperatures are given only for convenience and correspond to the cones as given in "Characteristics of Pyrometric Cones", by C. O. Fairchild and M. F. Peters, Jour. Amer. Cer. Soc., vol. 9, no. 11, p. 701, 1926.

The data obtained are given in table 1 and typical curves are given in figure 1. The average coefficient of expansion per degree centigrade between 20 and 900 C ranged from 0.0000106 to 0.0000118. The expansion of the natural material was measured on samples B, C, and F only. Rates of expansion were fairly regular except for slight irregularities between 200 and 300 C and again between 650 and 700 C approximately. These irregularities were more pronounced in samples C and F than in B. After heating at 1,400 C for 5 hours, the total expansion at 900 C for materials *B* and *C* was somewhat lower and the irregularity in the curve between 200 and 300 C was still noticeable, but no irregularity was evident in the rate of expansion above 300 C. The data in table 1 and the curve in figure 1 show that the linear thermal expansion of magnesite brick after having been heated at 1,400 C is somewhat greater than that of the olivines.

3. TRUE SPECIFIC GRAVITY

The specific gravities of the olivines were determined according to the A.S.T.M. standard method for specific gravity of pigments,[4] serial designation *D* 153–27, promulgated by the American Society for Testing Materials. Values obtained both on the raw materials and after heating them to 1,400 C for 5 hours are given in table 1. The specific gravity of calcined magnesite is included for comparative purposes. The values represent the average of three determinations (except sample *C*, raw, only two determinations) and in no case was there a greater variation from the average than ± 0.005. The range was from 3.206 to 3.436.

The specific gravity of samples *D* and *E* is higher when tested in the natural state than when tested after heating at 1,400 C. The other samples show higher values after heating when compared with the same material not heated. Both *D* and *E* have a high lime content and *D* apparently was fused after the preheating at 1,400 C.

4. PYROMETRIC CONE EQUIVALENTS (SOFTENING TEMPERATURES)

The pyrometric cone equivalents were determined according to the A.S.T.M. standard method, serial designation *C* 24–31,[5] and are given in table 1.

The P.C.E. of the three olivines from North Carolina was above 35 (under the conditions of the test cone 35 is approximately 1,785 C), the highest temperature conveniently obtainable with the furnace used, and showed no difference whether tested in the natural state or preheated at 1,400 C for 5 hours. The values of the others ranged from cones 11 to 33. The natural material and the same material preheated to 1,400 C did not give duplicate values, sample *D* being appreciably higher after preheating and *E* appreciably lower. Sample *F* gave only slightly different results with the natural and preheated specimens, but showed a very much higher shrinkage than the other samples during these tests. It was estimated that the cones after completion of the tests were only about one third their original size.

[4] American Society for Testing Materials Book of Standards for 1930, pt. II, p. 345.
[5] Described in American Society for Testing Materials Book of Standards for 1930, pt. II, p. 210.

5. LINEAR SHRINKAGE

The values for linear shrinkage of the olivines during heating at 1,400 C for 5 hours and given in table 1 should not be considered as exact, since the measurements were made on rather small specimens. Each of the results represents the average values of not less than three specimens. For purposes, however, of comparing the relative amount of shrinkage of the several samples during heating the values should be satisfactory. The olivines containing the highest percentages of calcium oxide show by far the greatest shrinkage. The shrinkage of the commercial magnesite appears low because the tests were made on calcined material, whereas the olivine specimens were made with the natural or untreated materials.

6. PETROGRAPHIC ANALYSES [6]

Petrographic analyses were made on the several olivines before and after the various heat treatments in order to obtain information relative to the effect of the various heat treatments on their composition. From the petrographic examination an estimation may be made of the relative quantities of forsterite and fayalite present in each of the samples. The results of the analyses follow:

Sample *A*. Webster, N.C.

Natural state.—Largely olivine. Impurity (approximately 15 percent) is largely serpentine. Optical properties of olivine indicate composition[7] to be 96 percent forsterite and 4 percent fayalite approximately.

Heated at 1,400 C.—Composed of olivine (pure or nearly pure forsterite) with minute dark colored inclusions along cleavage planes. The inclusions may be magnesio-ferrite, magnetite and hematite.

Heated to cone 32 (approximately 1,700 C).—Not greatly different from preceding sample.)

Sample *B*. Balsam Gap, N.C.

Natural state.—Largely olivine and less than 10 percent serpentine. Optical properties indicate about 95 percent forsterite and 5 percent fayalite approximately.

Heated at 1,400 C.—Very similar to sample *A* after the same heat treatment.

Heated at cone 34 (1,760 C).—Not greatly different from preceding sample except material is slightly magnetic.

Sample *C*. Franklin, N.C.

Natural state.—Largely olivine (92 percent forsterite and 8 percent fayalite approximately). Impurities consist of (*a*) approximately 5 percent serpentine, (*b*) approximately 5 percent of an unidentified material which may be magnetite, (*c*) very small percentages of a pyroxene and basic feldspar.

Heated to 1,400 C.

Heated to cone 33 (1,745 C).—Not greatly different from samples *A* and *B* after heating.

Sample *D*. Ludlow, Calif.

Natural state.—Largely olivine (90 percent forsterite and 10 percent fayalite). Impurities totaling approximately 10 percent consist of

[6] Made by Herbert Insley.
[7] See Winchell, Elements of Optical Mineralogy, pt. II, p. 168.

small amounts of (*a*) a monoclinic pyroxene, (*b*) isotropic crystals of what may be a spinel, (*c*) serpentine.

Heated at 1,400 C.—Olivine (pure or nearly pure forsterite) with abundant inclusions of (*a*) opaque particles (probably magnetite), (*b*) low index glass, (*c*) particles of what may be magnesio-ferrite. The material is slightly magnetic.

Heated to cone 16 (1,450 C).—Not greatly different from preceding specimen except material was nonmagnetic.

Sample E. Timothy Mountain, B.C.

Natural state.—Largely olivine (approximately 92 percent forsterite and 8 percent fayalite). Impurities consist of small amounts of (*a*) crystals of what may be a spinel, (*b*) opaque particles which may be hercynite.

Heated at 1,400 C.—Predominantly olivine. Contains small amounts of (1) high index particles of what is probably magnesio-ferrite, (2) opaque particles of what may be magnetite, (3) clinoenstatite, (4) glass. The material is slightly magnetic.

Heated at cone 30 (1,650 C).—Not greatly different from preceding specimens.

Sample F. Urals, Russia

Natural state.—Largely olivine (80 percent forsterite and 20 percent fayalite approximately). Impurities are present in small amounts as (1) serpentine and (2) opaque particles of an unidentified material.

{*Heated at 1,400 C.*
{*Heated at cone 32 (1,700 C).*—Olivine (pure or nearly pure forsterite) predominates. Impurities present were not definitely identified but indications point to presence of (1) magnetite, (2) hematite, (3) magnesio-ferrite, (4) glass. Crushed material is magnetic.

The principal result of heating the olivines to 1,400 C or higher was the apparent removal of the fayalite from the solid solution series (and its subsequent decomposition), leaving the olivines composed almost wholly of forsterite.

IV. DISCUSSION OF RESULTS AND PREPARATION OF BRICK

The refractoriness to heat of the olivines from North Carolina was such as to warrant the conclusion that they should prove suitable for use in certain industrial processes where a so-called special refractory material is desirable. Although the thermal expansion is high, it is somewhat lower than that of calcined magnesite. Burning shrinkage is very small compared with that of other refractory materials, consequently preheating or calcining of the material is not necessary before being manufactured into brick. The disappearance of the fayalite during heating apparently has no detrimental effect on the structure of material.

In order to determine the feasibility of preparing brick from olivine, a sample of run-of-mine material from North Carolina was crushed and sieved. The material used had the following sieve analysis: Through no. 6 sieve and retained on no. 14, 37½ percent; through no. 14 sieve and retained on no. 40, 37½ percent; through no. 40, 25 percent. A solution of gum tragacanth was added as the binder and the material was pressed into standard-size bricks in a laboratory

hand press, dried, and heated at approximately 1,425 C for five hours. The finished brick were well bonded and had a statisfactory appearance after the heat treatment. The following results of tests representing the average on three specimens are given so that some idea may be formed as to certain physical properties of the burned bricks: Modulus of rupture, 325 lb/in.^{2}; compressive strength, 5,250 lb/in.^{2}; absorption (by weight, 5 hour boiling), 12 percent, shrinkage (firing), 1.1 percent.

Crucibles were made by coring sections of the brick and filling them with a mixture of equal parts by weight of olivine, ground to pass a no. 100 sieve, and (1) flint, (2) ground magnesite brick, (3) low fusing portland cement, (4) alumina. Crucibles were made from a commercial magnesite brick and filled with similar mixtures, but the olivine in each case was replaced by magnesite. In addition, a crucible made from a silica brick contained a mixture of ground silica brick and olivine. The crucibles and materials were heated to and held at approximately 1,575 C for 1½ hours. The results of these slag tests, which are given in table 2, should be considered only as indicative and not as conclusive evidence of what might be expected because of the very limited amount of work done.

TABLE 2.—*Results of some slag tests with olivine and magnesite bricks* [1]

Olivine brick		Magnesite brick	
Nature of slag	Reaction	Nature of slag	Reaction
Olivine mixed with—		Magnesite brick mixed with—	
Potters flint	Strong [2]	Potters flint	Strong.
Calcined magnesite	Slight	Olivine	Slight.
Cement	Strong	Cement	Very slight.
Alumina	Slight	Alumina	Negligible.

[1] The mixture of olivine and finely ground silica brick on a silica brick showed very slight reaction.
[2] The crucible was directly in the path of the flame and the temperature to which it was subjected was much higher than that of the other crucibles. This was indicated by the fused and bloated appearance of the crucible and any result obtained would not be considered exactly comparable.

V. SUMMARY AND CONCLUSIONS

Samples of six olivines representing different deposits were studied in order to determine the suitability of this type of material for refractory purposes. The chemical analyses were obtained on the raw material, the linear thermal expansion, pyrometric cone equivalents (softening points), specific gravities, and petrographic analyses on both the raw material and material heated at 1,400 C. The following results were noted:

1. The chemical analyses showed the silica to range from 40 to 45 percent approximately, magnesium oxide 40 to 49 percent approximately, iron as ferrious oxide 7 to 15 percent approximately, and lesser amounts of alumina, calcium, and titanium.

2. The rate of thermal expansion was fairly regular from room temperature to 900 C except for slight irregularities between 200 and 300 C, and again between 650 and 700 C, approximately. These irregularities were less evident in the heated material than in the raw. The total expansion from 20 to 900 C ranged from 0.942 to 1.082 percent and is somewhat lower than that of magnesite.

3. The true specific gravity ranged between 3.206 and 3.420 for the raw material and between 3.294 and 3.434 for the material heated at 1,400 C. The specific gravity of the materials low in calcium oxide was decreased by heating.

The P.C.E. (softening point) of the raw ore ranged from 30 to above 35, except the material high in calcium oxide which varied from 11 to 16. The P.C.E. of the raw material was not necessarily the same as that obtained on the material after heating at 1,400 C.

4. The olivines from North Carolina were more refractory than those from the other sources.[8]

5. The petrographic examination indicated the material to be essentially olivine. The percentages of forsterite and fayalite varied quite appreciably with the respective olivines.

The results indicated that the material from North Carolina was sufficiently refractory to heat and some types of slag to warrant its use as a special refractory. Bricks were easily made from run-of-mine material and proved satisfactory in the few physical tests to which they were subjected.

WASHINGTON, October 28, 1933.

[8] U.S. Patent 1,926,094 has some bearing on the use of olivine in refractories and an anonymous article appearing in British Clayworker, 41 (484) 168 (1932), refers to certain magnesium silicates and patented processes incidental to their use or manufacture.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP646

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THE PHOTOGRAPHIC EMULSION: NOTES ON STABILITY OF FINISHED PLATES

By B. H. Carroll, Donald Hubbard, and C. M. Kretchman

ABSTRACT

The changes occurring in finished photographic plates on storage appear to be the result of continued after-ripening. The results are discussed with respect to variables known to affect this process. Existence of a critical region of bromide ion concentration was demonstrated and shown to be consistent with predictions from the silver ion-gelatin equilibrium. Formation of fog by adding acid to ammonia-process emulsions was confirmed and given a new explanation.

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I. INTRODUCTION

It is generally known that photographic sensitive materials gradually become developable without exposure ("chemical fog") and decrease in sensitivity; stability against these changes is an important property, which varies considerably with the type of material, and to a less extent with the make. Literature on the subject is scanty and qualitative; a good summary of the available information is given by Wentzel.[1] The data in this paper are not the result of a specific investigation of stability, but are rather an accumulation of tests on a considerable variety of experimental emulsions which were made under known conditions and stored together. The results, although incomplete, are at least an addition to the available literature.

The deterioration on storage appears to be primarily a continuation of the "after-ripening" process, going on at a much reduced rate because of drying and reduced temperature, and leading to practically the same consequences as excessive after-ripening by digestion. We have already [2] given data to show that unripened emulsions may undergo pronounced after-ripening on storage of the finished plates. If they have been thoroughly washed and coated without addition of soluble bromide the process is quite rapid; a great increase in sensitivity during the first 4 to 6 months is followed by deterioration which is under way within a year. The existence of this series of changes is

[1] Wentzel, Die Fabrikation der photographischen Platten, Filme und Papiere und ihre maschinelle Verarbeitung, vol 3, pt. 1, of Eder's Handbuch der Photographie 1930.
[2] Carroll and Hubbard, B.S. Jour. Research, vol. 7, (RP340), p. 219, 1931.

readily understood, as emulsion gelatins contain labile sulphur considerably in excess of the amount necessary to produce maximum sensitivity.[3] This gradually brings about excessive reaction of the silver bromide and the sensitizing compounds, with consequent fog and loss of sensitivity,[4 5] exactly as is observed from excessive after-ripening.

Deterioration on storage may have certain characteristics which are distinct from those of excessive after-ripening. Fog and desensitization may be caused by absorption of gases from the atmosphere, and by contact with the packing material; interference by either of these factors could readily invalidate experiments on other variables if storage conditions were not comparable. The fog on storage normally begins at the edges of the plates, and may be quite high for a few millimeters when the change in the center of the plate can barely be detected. This was first explained by Homolka,[6] by the migration of the soluble bromide in the emulsion during the drying process which normally begins at the edges. In case the drying is irregular, from badly designed plate racks or other causes of uneven air circulation, definite patterns may be formed on plates showing the positions of the eddies where drying was slowest.

In the last few years a number of organic compounds have been described [7] as preservatives for photographic materials. They are all of such character that complex formation with silver salts is probable, but experiments with nitrobenziminazol [8] have indicated that its effect on after-ripening is more than can be explained solely by the decrease in silver ion concentration which it produces.

II. EXPERIMENTAL

1. PROCEDURE

The experimental emulsions were all coated on glass, so that the effect of the support was reduced to a minimum. When old glass was used, the previous emulsion was removed by soaking in caustic-soda solution and scrubbing, and the plates were then soaked for at least a day in dilute chromic-acid solution before washing again and applying the substratum. The substratum consisted of emulsion gelatin 3.5 g per liter, hardened with chrome alum 0.3 g per liter; the plates were dipped in this solution and allowed to drain while drying. The finished plates were dried in a current of filtered air at 28 to 30 C, the humidity being kept down by recirculating it over ammonia coils, followed by electrical heating. The racks hold the plate only at the corners, slightly inclined to the vertical air stream; drying is quite uniform and usually complete in less than 3 hours.

The plates were stored in the same room with the drying cabinets. It is a basement room of relatively uniform temperature. During the summer the extremes of temperature and humidity do not reach it, but the temperature is almost never below 27 C for at least 3 months and frequently reaches 30°; during the winter it is normally about 20°. The plates were packed in the usual 3-part boxes after wrapping in

[3] Sheppard and Hudson, Ind. Eng. Chem. (Analytical Edition), vol. 2, p. 73, 1930.
[4] Sheppard, Phot. Jour., vol. 66, p. 399, 1926.
[5] Carroll and Hubbard, B.S. Jour. Research, vol. 11 (RP622), 1933.
[6] Homolka, Phot. Korr., p. 550, 1905.
[7] U.S. Patents nos. 1,696,830, 1,725,934, 1,758,576, 1,758,577, 1,763,989, 1,763,990; German Patent no. 558,419; Seyewetz, Phot. Korr., vol. 69, p. 67, 1933.
[8] Carroll and Hubbard, B.S. Jour. Research, vol. 9 (RP488), p. 529, 1932.

black paper obtained from a photographic manufacturer; plates where the emulsion had come in contact with the paper were discarded.

Test plates were developed in unbromided pyrogallol at 20 C. Test strips from the sector wheel sensitometer were brush developed for 3, 6, and 12 minutes. Plates exposed behind the Eder-Hecht wedge were tank developed under conditions roughly equivalent to the 6-minute brush development, although the dilute developer was more affected by bromide in the plates. Edge fog has been disregarded in the numerical data; the test strips were cut from the center of the plate, discarding a margin of at least 1 cm. From the total density, read in diffuse illumination with a Martens photometer, 0.06 has been subtracted for reflection by the support.

2. SOLUBLE BROMIDE

The procedure for testing the effect of soluble bromide has been to wash the emulsion thoroughly and then add the bromide in known amounts. In all recent experiments, the process has been controlled by determination of the bromide ion concentrations with the silver-silver bromide electrode. This can be strongly recommended for the purpose. Readings can be obtained in a few minutes with small samples. While the apparatus is more expensive and somewhat more delicate than that required for the conductivity method recommended by Wentzel, it has the great advantage that the readings are direct, and that there is no loss of sensitivity at low concentrations; a change in bromide ion concentration from 1×10^{-5} to $2\times10^{-5}N$ produces the same change in voltage as the change in concentration from 1×10^{-3} to 2×10^{-3}. It is therefore possible to detect significant changes in emulsions which have been washed too thoroughly to test by ordinary chemical methods. The complications in the washing process which are introduced by the combination of silver ions with gelatin have been discussed in some detail in previous papers.[9] [10] When it is necessary to use chemical methods for control, we have found the Volhard method (addition of excess silver nitrate and back titration with thiocyanate solution in the presence of nitric acid) much more satisfactory than the titration in neutral solution with chromate as indicator which is usually recommended.

The data are given in terms of the bromide ion concentration of the liquid emulsion, at 30 C wherever possible. It was found on using the electrode that the limit of the titration test for bromide is about $1\times10^{-4}N$, but that emulsions may be washed to $3\times10^{-6}N$ without producing an appreciable difference in fog in the freshly melted emulsion; the fog on digestion or storage is considerably affected by differences of this order. If to such emulsions soluble bromide is added in amounts of the order of 10 ml of 0.10 N solution per liter, the resulting bromide ion concentration may vary ±20 percent from the calculated $1.0\times10^{-3}N$ because of the presence in the emulsion of soluble bromide or "silver gelatinate", depending on the previous washing as already stated. This is not enough to be important photographically, but with smaller amounts of bromide the variation is to be taken into account. Wentzel recommends the addition of 8 to 16 ml of 0.10 N bromide solution per liter of emulsion; in the 1903 edition of the

[9] Carroll and Hubbard, B.S. Jour. Research, vol. 7 (RP376), p. 811, 1931.
[10] Carroll and Hubbard, B.S. Jour. Research, vol. 8 (RP430), p. 481, 1932.

Handbuch, Eder suggests 6 ml as the normal amount, with a range of 3 to 20 ml. In an emulsion containing 0.2 mol of AgBr per liter, this is a range of 1.5 to 10 molecules of soluble bromide per 1,000 AgBr, which corresponds well with present practice as determined by analysis of commercial emulsions.[11] Calculation taking into account the combination of silver ion with gelatin shows that in an emulsion containing 0.2 mol (38 g) AgBr per liter and no excess of either silver or bromide at pH 7, the bromide ion concentration is $2\times10^{-5}N$; with 1 KBr per 1,000 AgBr it is $2\times10^{-4}N$; and with 5 KBr per 1,000 AgBr it is $1\times10^{-3}N$.

Figure 1 illustrates the dependence of fog after 7 to 13 months storage on the bromide ion concentration of 4 typical emulsions. The various portions of each emulsion were treated identically except for the adjustment of bromide ion concentration just before coating

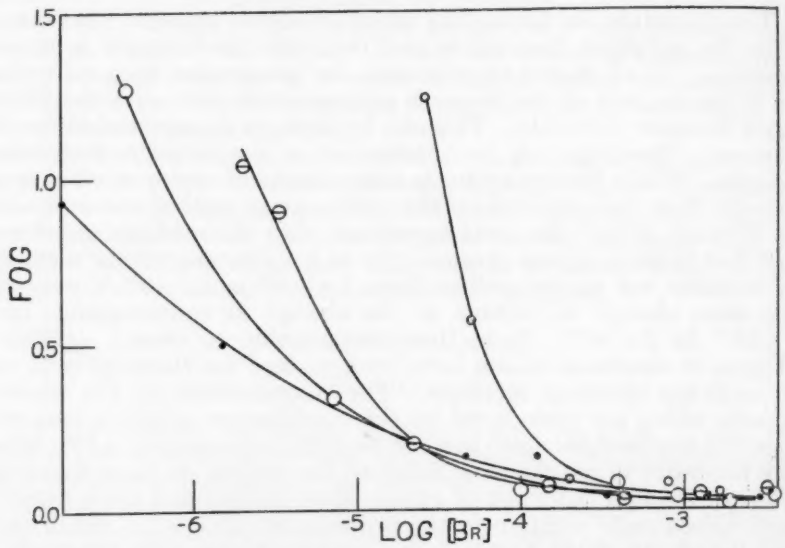

FIGURE 1.—*Stability of emulsions with varying bromide ion concentration.*

Fog, after 12-months storage, tank development, plotted against [Br⁻] measured in the liquid emulsion at 30.0 C. All emulsions of neutral type, 4 mol percent AgI. ○, 4-83, unsensitized, pH 6.4. ○, 4-108, pinaflavol sensitized pH 7.1. ⊖, 4-109, pinaverdol sensitized pH 7.1. •, 4-171, pH 6, sensitized with basic dye of unknown structure obtained by courtesy of Du Pont Film Mfg. Corp. (7 months storage only)

by addition of potassium bromide or silver sulphate solution. The data show clearly that a concentration of $2\times10^{-4}N$ bromide was sufficient to stabilize any of the emulsions. This is supported by the results of a number of earlier experiments, including ammonia-process emulsions with 0 to 2¼ percent AgI, in which it was found that the addition to the washed emulsion of 1 KBr per 1,000 AgBr was sufficient to prevent an increase in general fog of more than 0.05 in 6 months. This concentration does not prevent appreciable edge fog after 6 to 12 months. It is necessary to raise the bromide ion concentration to about $1\times10^{-3}N$ to avoid this; apparently the higher average concentration is necessary to maintain the first value out to the edges. If the emulsion is not sensitized by dyes, the sensitivity will not be appreciably affected by this increase,[12] and the higher

[11] Carroll and Hubbard, B.S. Jour. Research, vol. 10 (RP525), p. 211, 1933, table 1.
[12] Reference 10, (RP430), figure 7.

concentration is certainly preferable. In the case of panchromatic emulsions, the risk of edge fog in 6 or more months may be outweighed by the desirability of maintaining the maximum sensitivity, since the spectral sensitivity may be decreased by 20 to 50 percent on increasing the bromide ion concentration from 2×10^{-4} to 1×10^{-3}.[13]

The plates have been considered stable when the fog was less than 0.2 after the indicated period of storage and the sensitivity had not decreased appreciably. On after-ripening the sensitivity passes through a maximum, and may begin to decrease before or after the

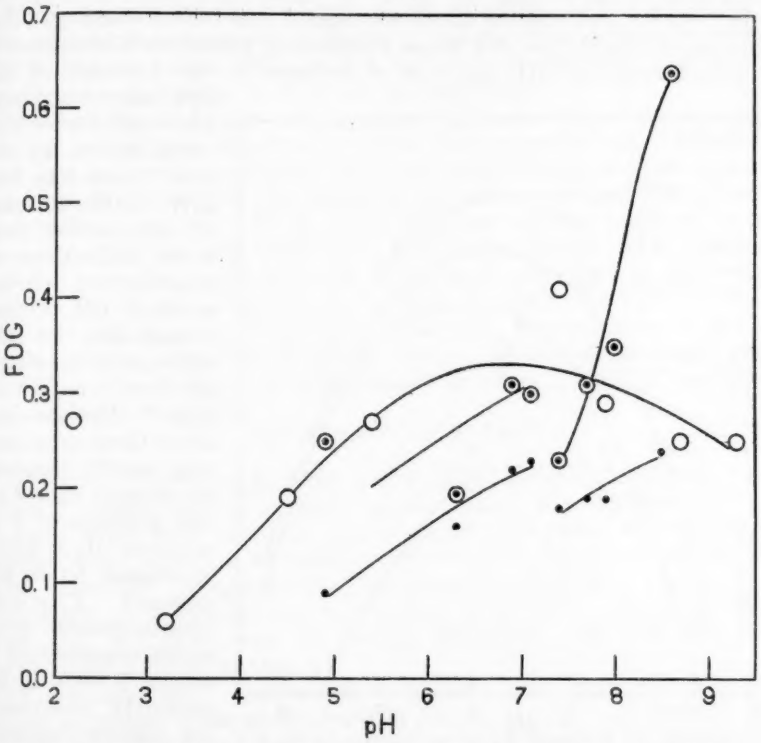

FIGURE 2.—*Stability of emulsions with varying hydrogen ion concentration.*

Fog after 12 months' storage, tank development, plotted against pH measured in the liquid emulsion. All emulsions of the neutral type. ○, 4-123, 4 mol percent AgI, pinaverdol sensitized [Br^-] 8×10^{-4} at pH 7.4. •, unsensitized emulsions, 2¼ mol percent AgI; pH 7.1 and less, emulsion 4-99, [Br^-] 1.0×10^{-4} at pH 7.1; pH 7.4 and over, emulsion 4-101, [Br^-] 1.3×10^{-4} at pH 7.4. ⊙ emulsions 4-99 and 101, pinacyanol sensitized.

appearance of serious fog, but fog as high as 0.5 invariably corresponded to a considerable decrease (about 50 percent). The definition of sensitivity also must be considered, since some plates which are nearly useless from fog and loss of contrast may still show high speeds by the threshold method. The emulsions of figure 1 were practically constant in sensitivity as judged by the Eder-Hecht exposure, if the bromide ion concentration was $1\times10^{-3}N$ or greater. At anywhere from 5 to $1\times10^{-5}N$ [Br^-] a decrease in sensitivity on storage set in, and the plates with the highest silver ion concentrations lost practically all sensitivity. Between these regions the

[13] Reference 8, (RP488), figure 6 to 9.

emulsions containing dyes were practically constant in sensitivity, while 4–83 doubled in speed at $10^{-4}N$ [Br^-]. In emulsions not thoroughly digested before coating there might have been much greater increases in sensitivity at about this point.

3. HYDROGEN ION CONCENTRATION

Increasing alkalinity strongly accelerates after-ripening[14] and may be expected to decrease stability of the finished plates. The effect is not as simple as this would indicate, however. Results with some neutral-process emulsions are given in figure 2; these were digested at pH 7.0 ± 0.1 and acid or alkali was added just before coating. The emulsions without dye and those containing pinacyanol increased in fog with increasing pH, the rate of increase in the presence of this dye being very large above pH 7 where the sensitization by the dye[15] also rose rapidly. In the presence of pinaverdol there were indications of maximum of fog around pH 7, corresponding to the flat maximum of sensitization by the dye.[16] The sensitivity of these emulsions was nearly constant on storage, except for the portions of 4–99 without dye, which increased 50 to 100 percent. The ammonia-process emulsions represented in figure 3 show a peculiarity discovered by Lüppo-Cramer,[17] the increase in fog on adding acid.

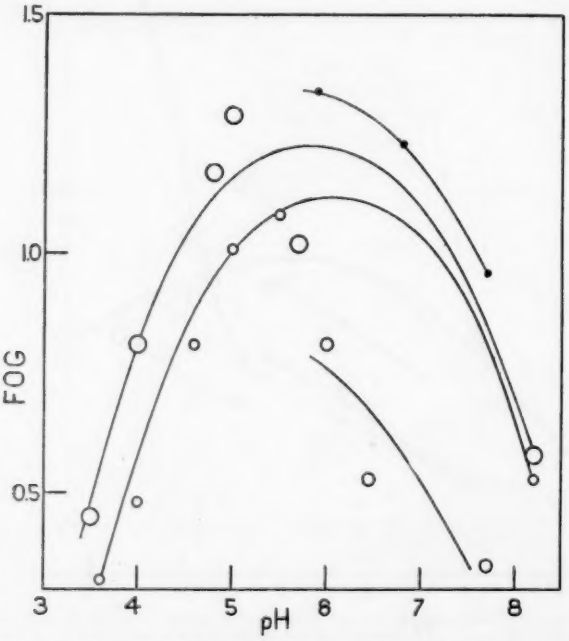

FIGURE 3.—*Stability of emulsions with varying hydrogen ion concentration.*

Fog after 6 months' storage, 6-minute brush development. All ammonia-process emulsions, 1 mol percent AgI, unsensitized. ○, 1-142, all portions digested at indicated pH. ◯, 1-144, all portions digested at pH 8.2 and brought to indicated pH just before coating. ○, 1-124, undigested. •, 1-125, portions digested at indicated pH.

We believe that this is explained by the increase in silver ion concentration which accompanies increase in hydrogen ion concentration of such emulsions. These emulsions had been washed until they contained an excess of silver over halogen, which was present in the form of a silver ion-gelatin complex. On acidifying, some of the silver ions were liberated; for example, a decrease in pH from 7.1 to

[14] Rawling, Phot. Jour., vol. 66, p. 495, 1926; vol. 67, p. 42, 1927; vol. 69, p. 83, 1929; also Carroll and Hubbard, reference 10.
[15] Reference 8 (RP488), figure 5.
[16] Reference 8 (RP 488) figure 4.
[17] Lüppo-Cramer, Phot. Ind., vol. 22, p. 186, 1924.

5.7 produced an increase in silver ion concentration of 5 times. This decreased the stability by an amount much larger than the opposing effect of the change in hydrogen ion concentration. This explanation would apply not only to emulsions made by the ammonia process but also to plates made by the neural process and bathed in ammonia or other alkali as in Lüppo-Cramer's experiments. Below pH 6 the stabilizing effect of hydrogen ion concentration begins to become the more important. At a pH of 3 an emulsion may be stable in the presence of an appreciable excess of silver over halogen; as would be expected, this acidity decreases sensitivity by a serious amount. At the lowest values of pH (<4) the sensitivity of the emulsions represented in figure 3 was nearly constant on storage. At all higher values there was a decrease in contrast and effective sensitivity amounting to as much as one half.

The poorer stability of ammonia-process emulsions is not as marked as is to be anticipated from their reputations. When neutral and ammonia emulsions with the same iodide content are compared at the same pH and bromide ion concentration, the difference is apparently small. These conditions are seldom fulfilled in practice, since after normal washing in hard water the pH of an ammonia-process emulsion is likely to be 8.0 to 8.5, and that of the neutral-process emulsion 7.0 to 6.5. Further, because the combination of gelatin with silver ions increases with pH, the washing of the ammonia-process emulsion proceeds further in the same time; and in addition to this most formulas direct a more thorough washing to eliminate the ammonia.

4. OTHER VARIABLES

The entire ripening process under given conditions becomes more rapid with decreasing proportion of iodide; the difference is most marked when pure bromide emulsions are compared with those containing small amounts of iodide. Increase in fog on storage is, however, relatively independent of the amount of iodide; pure bromide emulsions were appreciably less stable than those containing 2 percent AgI, but there was no certain difference produced by further increases in iodide content.

Of the sensitizing dyes which were used, only pinacyanol at a pH above 7 tended to cause increase in fog on storage; erythrosin, pinaverdol, and pinaflavol had no effect or even tended to preserve the plates in spite of their tendency to cause fog directly after their addition. All the dyes stop storage ripening of undigested emulsions almost completely.

In general, the increase in fog on storage is less in emulsions which have been digested, provided the digestion was not carried past the optimum sensitivity. This is especially noticeable in emulsions digested and coated without addition of soluble bromide after washing. We have previously observed this [18] and offered a tentative explanation.

Emulsions prepared with deactivated gelatin and allyl thiocarbamide showed normal after-ripening on storage, if not digested to equilibrium. The fog was low (not over 0.1 on the tank development after 1 year) in emulsions with a ratio of 4×10^{-5} g equivalent of

[18] Reference 2 (RP340).

sensitizer per g equivalent of AgBr (or less), [Br^-] of emulsion 5×10^{-5}. With double this amount, the fog increased to about 0.2 and with 12 or 16×10^{-5} ratio, deterioration was serious.

III. DISCUSSION

The results are in accordance with the theory stated in the introduction, that deterioration on storage is the consequence of continued after-ripening; that is, of continued reaction between the silver halide and the sensitizing and fogging constituents of the gelatin. Some of its characteristics may be better understood by considering the probable changes on drying the emulsion. The water content is thereby reduced from about 15 times the weight of the gelatin to about one seventh of the latter, or a reduction to approximately 1 percent of its original amount. Materials in solution in the emulsion will thus be greatly increased in concentration. Acid or alkali in small amounts will be an exception to the expected result because gelatin has the characteristic common to good "buffers", that its pH is little affected by concentration. Soluble bromide must, however, be much more concentrated in the dried emulsion than in the state where its concentration was measured for these experiments. The adsorption of soluble bromide by silver bromide may be expected to reach a condition of practical saturation at some concentration of the former. The data suggest that this is something over 0.02 N, since the stability is little improved by further addition of bromide above that necessary to produce 0.0002 N in the liquid emulsion. With smaller amounts, the change in concentration on drying is considerably affected by the combination of silver ions with gelatin. At pH 7 and [Br^-] 2×10^{-5} N, the emulsion contains no excess of silver or halogen; in solution the free bromide ions are in excess of the free silver ions, but the silver ions conbined with the gelatin are equivalent to this excess. Therefore, on drying, the bromide ion concentration will remain practically unchanged, since there is essentially a solution of silver bromide in gelatin solution; the net effect will be crystallization of solid silver bromide from solution, since the gelatin will give up silver ions to a solution of higher bromide ion concentration. It is possible, then, that on drying an emulsion with an initial [Br^-] of 2×10^{-5} N, the final value shall be the same, while starting at [Br^-] 2×10^{-4} N it rises to 2×10^{-2}, so that this region is one of rapid change in stability.

Washington, September 16, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP647

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A PORTABLE ULTRAVIOLET INTENSITY METER, CONSISTING OF A BALANCED AMPLIFIER, PHOTOELECTRIC CELL, AND MICROAMMETER

By W. W. Coblentz and R. Stair

ABSTRACT

A description is given of the construction and performance of a portable ultraviolet intensity meter, consisting of a photoelectric cell (of titanium, uranium, cadmium, etc.), a balanced amplifier circuit, and a comparatively insensitive microammeter.

A means is described for testing the constancy of the sensitivity of the amplifier.

It is found that, after preliminary operation for 5 to 10 minutes, to attain temperature equilibrium in the amplifier tubes, there is no fluctuation in the zero scale reading of the microammeter either when testing the amplification sensitivity of the instrument, or when making measurements of ultraviolet intensities, of the sun and of artificial sources, by means of the photoelectric cell.

The indicator response (scale reading) was found linear within the accuracy of the microammeter used.

Owing to the selective wave length response of the photoelectric cell, this device, like all selective radiometers, is calibrated in absolute value, by means of the standard balanced thermopile and filter radiometer ("differential actinometer") described in RP370 and RP450.

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I. INTRODUCTION

Since the advent of the thermionic ("radio") tube, about 3 decades ago, a number of arrangements of electric circuits have been proposed for amplifying small unidirectional electric currents, such as are obtained from thermopiles and photoelectric cells.

However, but few of these proposals have survived; and only within the past few years has substantial progress been made in devising means for the precise amplification and measurement of the small electrical currents available in radiometry.

This is owing partly to the general complexity and instability of the electronic circuit (which is sensitive to electrostatic disturbances), and partly to the lack of provision for electrically standardizing the amplifier—a necessary procedure since there is no convenient source of ultraviolet, of sufficient constancy, for use as a standard in calibrating the combined radiometer (photoelectric cell) and radio amplifier.

The situation is somewhat similar to that experienced in connection with the use of a thermopile connected with a Thomson galvanometer (8).[1]

[1] Figures in parenthesis here and throughout the text indicate references and notes given in the bibliography at the end of this paper.

Owing to the varying current sensitivity of the galvanometer, the scale reading is evaluated, at frequent intervals, by means of an auxiliary electric circuit (consisting of a dry battery and suitable resistances) which provides a constant electric current, of an arbitrarily chosen magnitude that insures accuracy in reading the galvanometer scale.

Since the radiation sensitivity of the thermopile (in air) is subject to but little, if any, change with usage, the combination (consisting of the thermopile and galvanometer) is calibrated, at infrequent intervals, in absolute units, by means of a standard of radiation (2).

Based upon the results obtained in standardizing the Thomson galvanometer scale reading (8), in the present investigation a somewhat analagous procedure was adopted for calibrating the combined amplifier and microammeter scale reading—the microammeter, by itself, being subject to practically no variation in sensitivity. That is to say, the constancy of the scale reading of the microammeter, when used in connection with the radio amplifier (but separate from the photoelectric cell), is determined by means of an auxiliary electrical circuit (consisting of a voltmeter, dry battery, and resistances) so arranged that, when an arbitrarily chosen but constant emf is impressed upon the amplifier, the microammeter scale reading is a convenient magnitude that can be read accurately.

Since, as already mentioned, there is, as yet, no simple standard of ultraviolet radiation for accurately testing the constancy of the photoelectric cell (which is subject to a slow change in sensitivity with usage) it is desirable to provide several cells, one or more of which are kept in reserve and used infrequently as standards, for testing the constancy of the cells that are in regular use.

The microammeter scale reading, for the complete assembly (photoelectric cell, amplifier, and microammeter, etc.) is calibrated in absolute units by means of a standard balanced thermocouple and filter radiometer, or so-called "differential actinometer" (1). Such a calibration is necessary for each type of source used in ultraviolet radiation therapy.

In a previous communication (1) a description was given of the calibration, in absolute units, of a portable Rentschler ultraviolet meter, which consists of a titanium or uranium photoelectric cell, connected with an electron discharge tube and an automatic counting device. By using a number of photoelectric cells, all intercompared (when new) against a source of ultraviolet, then several kept in reserve as standards, it was possible to determine (without reference to a standard source of ultraviolet) whether a certain photoelectric cell or the electron discharge tube had changed with prolonged usage.

In the present communication a description is given of the performance of a portable ultraviolet intensity meter, consisting of a photoelectric cell (of titanium, uranium, cadmium, sodium, etc.,) connected to a balanced amplifier circuit (which is essentially a Wheatstone bridge), and a relatively insensitive microammeter. No attempt is made to use a balanced photoelectric cell circuit (3) by connecting two photoelectric cells in opposition (thus completing the analogy with the balanced thermocouple and filters), (1), because the additional complications do not appear to be necessary to meet our present requirements.

While but little novelty can be claimed for present-day amplifier circuits, involving the Wheatstone bridge principle (4), the manner in which the present amplifier device was worked out (principally by Stair) to meet the foregoing specifications, and the manner of testing the constancy of the amplification, is described in the following caption.

II. DESCRIPTION OF THE ELECTRIC CIRCUIT

The amplifier circuit, shown in figure 1, is essentially a Wheatstone bridge in which the arms R_1 and R_2 are two similar resistances (each of 100,000 ohms), and the arms T_1 and T_2 are two vacuum tubes

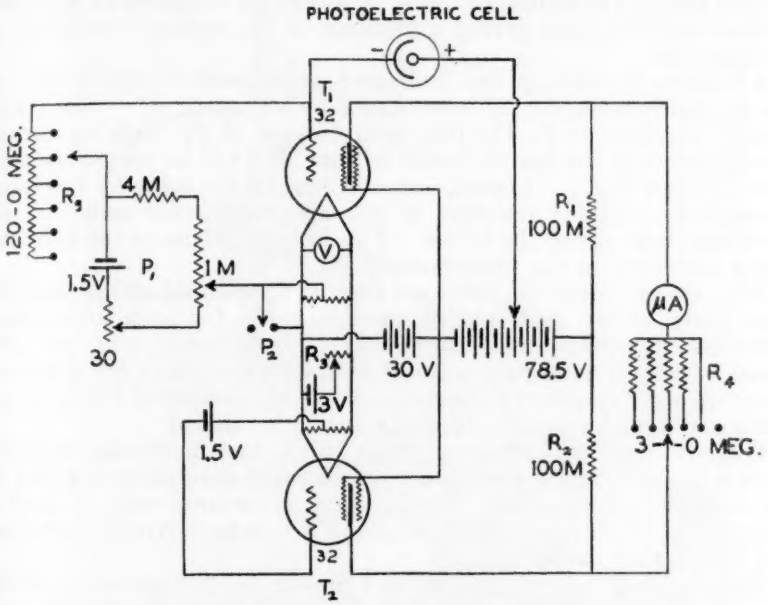

FIGURE 1.—*Wiring diagram.*

(type 32, screen grid), which are as nearly identical as can be obtained commercially.

The pair of tubes employed were chosen after an examination of the characteristic curves of a number of tubes of this type. Contrary to some writers, there was no difficulty in finding pairs (or triplets) of tubes having practically identical characteristics; and the characteristics of these pairs are so closely the same that they can be interchanged in this assembly without modification of the resistances in the circuit. These pairs and triplets are, therefore, being held in reserve for replacements.

The use of matched vacuum tubes is a further modification of the electric circuit originally developed by P. I. Wold; improved by Wynn-Williams, by Eglin, and by Razek and Mulder; and recently discussed in detail by Nottingham (4).

In the present circuit, the grid potential of the tube, T_2, is placed at a fixed negative value, in the region of the flat portion of the positive ion, grid current curve; and near the lower end of the straight portion

of the plate current vs. grid voltage curve of the particular tubes used. This is in contrast with the floating grid, or semifloating grid potential often used. The use of the type 32 screen grid tube greatly reduces the grid current difficulties in an amplifier of this type.

Since the grid of the tube T_2 is at a fixed potential, and that of T_1 is always adjusted to a similar value, by means of the potential varying device P_1, the voltage sensitivity of the amplifier remains the same regardless of the resistance, R_g. This is not the case where the grid potential of the tube, T_2, also changes, as occurs with a change of grid resistances, used for increasing the current sensitivity.

In order to test the amplifier sensitivity from day to day, the potential changing device, P_2, is incorporated. By means of this control the grid potential of the tube T_1 can be changed, at will, by a definite amount, thus giving a measure of the voltage sensitivity of the amplifier.

A balance of the amplifier (indicated by no current flowing through the microammeter, fig. 2) is obtained by adjusting P_1. Since T_1 is closely identical to T_2, the final grid voltage of T_1 (with no current flowing through the photoelectric cell and R_g) will be very closely the same as that of T_2. It could be made exactly the same by the incorporation of variable resistors in the filament circuit and (or) the plate circuit of one of the tubes. This latter refinement has not been found necessary in the present work.

Since closely identical tubes are used in a balanced circuit with the same plate, screen grid, and filament batteries for both tubes, small variations in voltage are unimportant. Furthermore, since no additional battery is necessary in connection with the use of the microammeter or other sensitive indicating device, the danger of injury to the meter is avoided when the filament circuit is opened.

The dry batteries, resistors, radio tubes, and meters are mounted upon a chassis, which includes a hard-rubber insulating support for the control switches, etc. This support is covered with a sheet of aluminum, suitably perforated to permit access to the control switches, and for viewing the meters.

The complete assembly is inclosed in a metal box, as shown in the photograph, figure 2, for protection against electrostatic disturbances. A further elimination of electrostatic variations is obtained by covering the binding post, connected with the control grid of the active radio tube, with a metal cap, no. 7, figure 2. Inclosing the photoelectric cell in a metal housing is also desirable to reduce electrostatic disturbances when making measurements out of doors when there is a strong wind.

The controls indicated in figure 2, serve the following purposes: nos. 1 and 3 (P_1 in fig. 1) are commercial resistances of 1,000 and 30 ohms (for coarse and fine adjustment), respectively, for regulating the control grid voltage of the active tube, in order to adjust the microammeter (to right in fig. 2) to the zero scale reading; no. 2(R_3 in fig. 1) is a radio rheostat of about 25 ohms for regulating the filament voltage (set at 1.9 volts) as indicated on the voltmeter, to the left in figure 2; no. 4 (R_4 in fig. 1) consists of a group of resistors arranged for reducing the sensitivity of the microammeter, and thus protecting the meter while the preliminary adjustments are being made; no. 5 (R_g in fig. 1) is similarly connected with a group of high grid resistances, for controlling the current sensitivity of the instru-

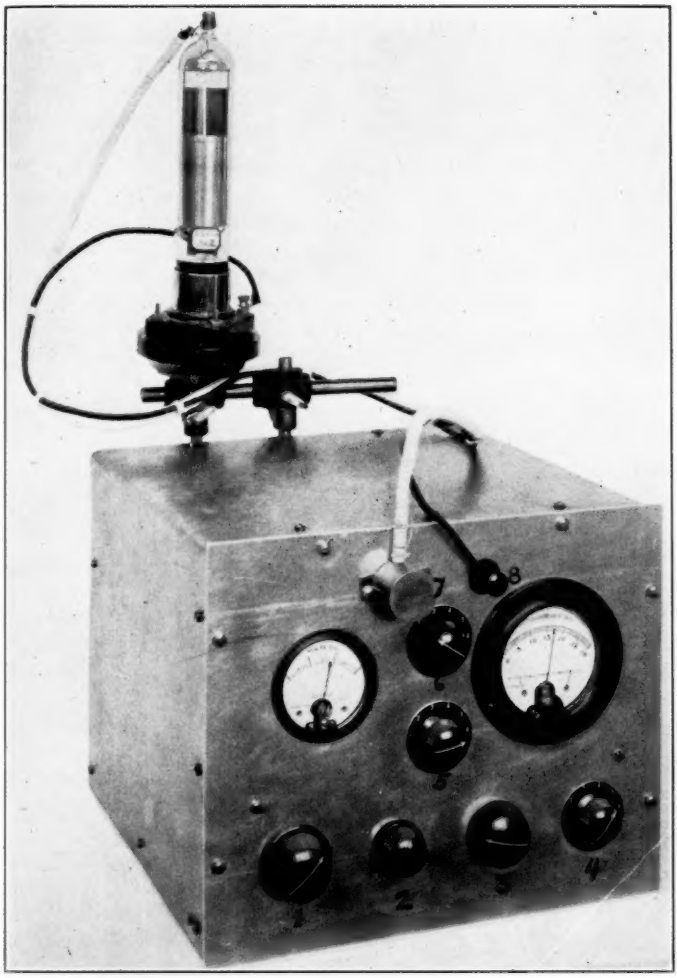

FIGURE 2.—*Portable ultraviolet intensity meter.*

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ment (i.e., for controlling, in five steps, the current through the micoammeter when the photoelectric cell is irradiated; and no. 6 (P_2 in fig. 1) is used for determining the voltage sensitivity of the amplifier, which is read as an arbitrary deflection on the microammeter.

Since a suitable shielded cable was not available for connecting the photoelectric cell to the amplifier (nos. 7 and 8, in fig. 2) one was constructed. For the cathode lead an ordinary lamp cord wire was drawn through a section of heavy rubber tubing and this wrapped with no. 26 cotton-covered copper wire, which was grounded to the metal box. Shielding of the anode wire is unnecessary since it has a definite potential and low impedance to ground. The photelectric cell support (when not mounted on the amplifier box) is connected to the box by means of an auxiliary grounding wire.

For the use of this instrument as an ultraviolet (dosage) intensity meter, employing commercially available photoelectric cells, and applying it to various sources of ultraviolet in use, it was found that an overall range in current amplification of 100 to 20,000 was sufficient for all practical purposes. Higher or lower ranges of amplification could be easily obtained by using higher or lower values of R_g (fig. 1), or by using a more or less sensitive indicating meter.

The constancy of the resistors (R_g in fig. 1) is determined, from time to time, by comparison with our standard Thomson galvanometer sensitivity testing device (8).

III. PERFORMANCE TESTS

Using a balanced thermopile and filter radiometer, (calibrated against a standard of radiation) (2), and data on the spectral energy distribution of the source, it is possible to evaluate the ultraviolet in different sources in absolute units. This instrument is therefore used as a primary standard (6) for calibrating selective radiometers (photoelectric cells) in absolute value. Such a calibration of the indicator (microammeter, in the present case) scale of an ultraviolet (dosage) intensity meter is necessary for each kind of source used.

For example, using a certain kind of photoelectric cell, insensitive to ultraviolet of wave lengths longer than 334 $m\mu$, in a Corex *D* glass bulb, which is opaque to radiation of wave lengths shorter than 280 $m\mu$, the factors for converting the microammeter scale reading into microwatts per square centimeter of radiation of wave lengths shorter than 313 $m\mu$, were 1.94, 12.4, and 18.5, respectively, for the sun, the *S*-1 lamp and the "Therapeutic C"–carbon arc lamp.

The large factor for the "C"–carbon arc is owing to the large amount of radiation in the spectral region of 220 to 260 $m\mu$, emitted by the lamp (6) but excluded from the photosensitive material contained in the glass bulb, which is opaque to radiation of wave lengths shorter than 250 $m\mu$.

Photoelectric cells of titanium, uranium, cadmium, etc. (7) which are insensitive to radiation of wave lengths longer than about 330 $m\mu$, appear to be applicable to the measurement of the short wave length ultraviolet of a greater variety of sources than the photoelectric and "photronic" cells, which have their maxiumm response in the visible spectrum, and are sensitive to the near infrared. The latter type, however, is simpler to operate and is satisfactory where high precision is not required.

The necessity of calibrating the photoelectric cell, in absolute value, against a standard nonselective radiometer is unavoidable. Accepting this as necessary for all selective radiometers the two outstanding desiderata are; (*a*) that the indicator of the ultraviolet dosage intensity meter shall have a stable zero reading and (*b*) that the scale reading shall be linear. An instability of the zero reading may be owing to electrostatic disturbances, and to temperature changes in the amplifier.

Performance tests, made in the field and in the laboratory, show that the indicator (microammeter), of the herein described ultraviolet intensity meter, has a stable zero reading, after it has been operated for 5 to 10 minutes, to permit the temperature of the amplifier tubes to come to equilibrium. During this interval the voltmeter setting (1.9 volts) may increase by a perceptible amount that is eliminated by readjustment of the rheostat, R_3 in figure 1.

After this preliminary adjustment to equilibrium, no shifting of the zero of the indicator (microammeter) occurred either when testing the amplification sensitivity of the instrument (by unbalancing the circuit by means of the switch P_2 in fig. 1), or when making measurements of ultraviolet intensities by means of the photoelectric cell.

The linearity of the indicator (microammeter) scale reading was found accurate within the tolerance (± 1 percent) in accuracy of the particular microammeter used. This is higher than is required relative to the constancy of the ultraviolet output of the sources in common use; especially of sunlight, at sea level, which is subject to large fluctuations in intensity with slight changes in atmospheric conditions. Hence, for all practical purposes, nothing would be gained by using a null method for measuring the photoelectric current.

In conclusion, it is relevant to add that, in this preliminary study, the indicator employed was an inexpensive microammeter (Weston, model 600), which is sufficiently accurate for ordinary use. Placed in a vertical position, as indicated in figure 2, the needle was slightly unbalanced, producing slight irregularities in the scale reading. As a highly accurate measuring instrument, for investigating atmospheric transmission coefficients, etc., it is proposed to replace the present indicator by a precision microammeter (Weston, model 440), used in a horizontal position in order to take full advantage of the highest accuracy that is attainable.

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WASHINGTON, December 14, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP648

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

NOTE ON PHASE EQUILIBRIA IN THE SYSTEM Na_2O–TiO_2

By Edward W. Washburn and Elmer N. Bunting

ABSTRACT

The following compounds are formed in the binary system Na_2O–TiO_2: Na_2TiO_3 melting at 1030 C, $Na_2Ti_2O_5$ melting at 985 C, and $Na_2Ti_3O_7$ melting at 1128 C.

As a part of the Bureau's program of research on phase equilibria in systems containing refractory oxides, it had been planned to study a variety of systems containing TiO_2 as one of the components, since this interesting oxide has in recent years become commercially available in large tonnage and in a remarkably high state of purity. The first investigation dealing with the different crystalline forms of TiO_2 itself and with equilibria in the systems TiO_2–SiO_2 and TiO_2–Al_2O_3 has been completed and published.[1] With the inauguration of the economy program on July 1, 1933, it became necessary to abandon research work in this field.

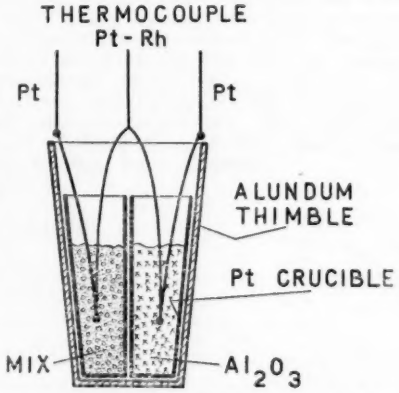

FIGURE 1.—*Twin Pt crucibles in alundum thimble for determining heating curves.*

The purpose of the present note is to place on record a few results which have been secured in an incomplete study of the system Na_2O–TiO_2. Mixtures of these two oxides were found to crystallize so readily that it was not necessary to employ the laborious quenching method; in fact it could not be used on account of the rapidity of crystallization. Instead, the method of heating curves was employed. The essentials of the method as applied to these mixtures will be clear from the accompanying diagram. The results indicated the formation of three compounds with congruent melting points as follows: Na_2TiO_3 melting at 1030 C, $Na_2Ti_2O_5$ melting at 985 C, and $Na_2Ti_3O_7$ melting at 1128 C.

WASHINGTON, October 28, 1933.

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U.S. Department of Commerce, Bureau of Standards

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COMPARATIVE EFFICIENCIES OF VARIOUS DEHYDRATING AGENTS USED FOR DRYING GASES (A SURVEY OF COMMERCIAL DRYING AGENTS)

By J. H. Bower

ABSTRACT

This paper discusses the various types of drying agents and their different modes of functioning. The method employed for determining the comparative efficiencies of the more common commercial drying agents as well as some newer drying materials recently introduced, was to aspirate properly conditioned air through a train of U-tubes containing the drying materials in the order of their increasing drying powers. After a measured amount of air had passed through the system, the increase in the weights of the U-tubes following any one U-tube indicated the residual water escaping that tube. The materials studied (with the amount of residual water in milligrams per liter of air dried), in the order of increasing efficiency at 30 C, follow: $CuSO_4$ (anhydrous) (2.8); $CaCl_2$ (granular) (1.5); $CaCl_2$ ("Techincal anhydrous") (1.25); $ZnCl_2$ (sticks) (0.98); Ba $(ClO_4)_2$ (0.82); NaOH (sticks) (0.80); $CaCl_2$ (granular) (dehydrated) (0.36); Mg $(ClO_4)_2.3H_2O$ (0.031); Silica Gel (0.030); KOH (sticks) (0.014); Al_2O_3 (0.005); $CaSO_4$ (anhydrous) (0.005); CaO (0.003); Mg $(ClO_4)_2$ (0.002); BaO (0.00065).

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I. INTRODUCTION

Drying agents are utilized in the laboratory for the drying of gases and liquids by direct action (contact) and for the drying of solids (and liquids) by indirect action (through the intermediary of a gas, liquid, or an evacuated space). For the purpose of discussing the action of the various types of drying agents which are commonly used in the laboratory, it will be convenient to recognize five classes.

II. CLASSIFICATION OF AGENTS

A. CLASS 1

Drying agents whose efficiency is determined primarily by a chemical reaction of the type:

$$A(H_2O)_y \text{ (solid)} + xH_2O = A(H_2O)_{x+y} \text{ (solid)}.$$

The drying power of such an agent, when used under equilibrium conditions (for example in a desiccator) is measured by the equilibrium pressure of the water vapor, which pressure is a characteristic of the reaction at any given temperature. The corresponding limiting capacity of the drying agent per mole of $A(H_2O)_y$ is x moles of water. The practical capacity will be something less than this value. The ordinary granular calcium chloride "for desiccators" is a drying agent of this class. The reaction, applicable to the reagent used in the present work, is

$$CaCl_2H_2O + H_2O = CaCl_2(.2H_2O).$$

The equilibrium pressure of water vapor is 13 mm Hg at 65 C (19).[1]

B. CLASS 2

Drying agents whose efficiency is determined by a reaction of the type:

$$A(\text{solid}) + H_2O = \text{saturated solution}$$

The drying power is measured by the equilibrium pressure of water vapor for this reaction and the drying capacity will vary inversely as the solubility of A. Common salt is a drying agent of this character. Drying agents of this class find their principal use in humidity control.

C. CLASS 3

Drying agents whose efficiency is determined by a reaction of the type:

$$A(\text{liq.}) + H_2O = \text{solution}$$

The drying power of this class of drying agents decreases continuously as water is absorbed. In order to avoid this progressive decrease in drying power, drying agents of this class are usually applied in cascade or in counter-current flow. Sulphuric acid is an example of this type of drying agent.

D. CLASS 4

Adsorption drying agents of which silica gel is an example, depend for their drying efficiency on a large effective exposed surface together with a sufficient adsorptive capacity for water vapor. When used in a tube or tower the drying power may be very great. The drying capacity per unit surface is usually small and to be of practical value this class of drying agents must have a large effective surface. The drying capacity of a given exposed surface decreases continuously with the adsorption of water. Drying agents of this class are, therefore, usually disposed in tandem fashion as in a tube or tower, and must be renewed for each experiment. Drying agents of class A, when in granular or finely powdered condition, function partially through adsorption when used in tandem fashion and consequently may have in practice, when fresh, a higher drying power than that corresponding to the equilibrium pressure characteristic of the chemical reaction. Also a drying agent of class A may under appropriate conditions function solely as an agent of class D.

[1] The numbers, 1 to 23, in parentheses in the text and table refer to the references, p. 248.

E. CLASS 5

Drying agents which decompose water are exemplified by the alkali and alkaline earth metals and their alloys. If the hydrogen resulting from the decomposition of the water can be continuously and completely removed, the drying power of this class of agents is practically infinite. In any case, it is determined by the partial pressure of hydrogen in the dried gas (or from the dried liquid) which is in equilibrium with a clean surface of the metal and by the value of the equilibrium constant of the reaction

$$M + (H_2O)_x = M(OH)_x + \frac{x}{2}H_2$$

Three of the most important properties of drying agents for laboratory purposes are the following: (*a*) drying power, that is, completeness of water removal; (*b*) drying capacity, that is, amount of water which can be removed by unit mass without loss of drying power or in some cases without decrease of drying power below some stated limit, and (*c*) speed of drying under the conditions of use.

Since the purpose of this survey was to compare the efficiencies of the various agents when used to dry a gas stream by a commonly used laboratory procedure, the results reported should be understood to pertain to approximately equilibrium conditions. No attempt has been made to determine the ultimate drying power, that is, the residual moisture corresponding to complete equilibrium. Where this latter information is available in the literature, however, it has been reduced to the same units and is inserted in the table for comparison. No study has been made of the capacity of the materials or limiting rates of air flow.

III. METHOD EMPLOYED

Properly conditioned air was aspirated through a train of U-tubes containing the desiccating materials to be studied. These materials were arranged in the order of their drying powers with the final tube or tubes containing material such as phosphorus pentoxide. The total gain in weight in all tubes following any one tube, therefore, represented the residual water escaping that tube.

In detail, the whole apparatus consisted of a constant-temperature cabinet containing a wet gas meter followed by a drying tower charged with two layers of "dehydrite" enclosing a layer of "ascarite" (NaOH-asbestos mixture). From the drying tower, connection was made to a 200 mm U-tube containing $Ba(OH)_2.8H_2O$ crystals to supply a suitable amount of water.[1] This tube was followed by the 100 mm U-tubes (see fig. 1) containing the various desiccants. All connections beginning with the drying tower and up to the final U-tube were ground joints (fig. 1). A lubricant of negligible vapor pressure was used on these joints and all connections were coated with a layer of wax (rosin and beeswax).

The outlet of the final tube was connected, by means of heavy-walled rubber tubing passing through the end of the cabinet, to a guard tube containing phosphorus pentoxide and this in turn was connected to a flask containing concentrated sulphuric acid, and, through this to a mercury manometer and a filter pump.

[1] The average equilibrium pressure at 30.5° was found to be about 11.3 mm.

Constant temperature was maintained by the use of two 100-watt bulbs, a bimetallic thermoregulator,[2] an electric fan and a storage battery. The temperature in the cabinet was maintained at 30.5° ± 0.5 C so as to be able to operate during the summer months. Runs were made only during the day, all stopcocks being closed at night. The rate of air flow varied from 1 to 5 liters per hour in most experiments. The internal pressure of the system was determined in each case. However, corrections for differences in the volumes of air entering and leaving the system were found to be negligible.

IV. MATERIALS USED

Except as otherwise noted the materials studied were commercial products in the form in which they were marketed as drying agents. In most cases they are identified below only by information taken from the label of the container. In some instances, however, a partial analysis was made and the results are indicated. Before use, certain of the drying agents were first subjected to a dehydrating treatment corresponding to that normally employed in preparing them for use or in regenerating them. Such treatments are indicated in each instance.

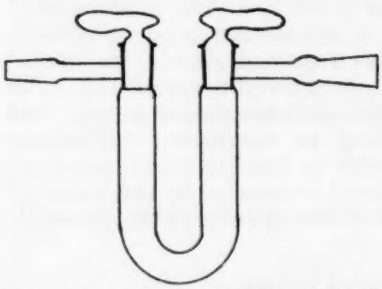

FIGURE 1.—*Type of U-tube employed.*

"Anhydrous Copper Sulphate" was the "C.P." powder. Analysis gave 92.5 percent of $CuSO_4$. The tube of copper sulphate was heated to 250 C for 2 hours while passing through it air dried by phosphorus pentoxide. "Calcium Chloride (Granular)" was labeled "anhydrous (dried) granular for drying tubes," and was of 8-mesh fineness. The analysis showed the average composition to correspond approximately to $CaCl_2.H_2O$. "Calcium Chloride (Technical Anhydrous)" was found by analysis to have an average composition corresponding to the formula $CaCl_2.\frac{1}{4}H_2O$. "Zinc Chloride (Sticks)" was the "C.P." material. Analysis showed 97.9 percent of $ZnCl_2$. "Barium Perchlorate (Anhydrous)" or "Desicchlora" was a commercial product and was in the form of irregularly shaped lumps varying in size. "Sodium Hydroxide (Sticks)" was the "C.P." material. The analysis showed 97.1 percent of NaOH and 0.6 percent of Na_2CO_3. It was crushed to a coarse powder for use. "Calcium Chloride (Anhydrous)" was the granular calcium chloride previously described, which had been heated to 250 to 275 C in the U-tube, while passing through it air dried by phosphorus pentoxide. The dry air was followed by dry carbon dioxide to neutralize any basic compounds present. "Magnesium Perchlorate-Trihydrate" or "Dehydrite" was a commercial product and was in a coarsely granular form. "Silica Gel" was a granular commercial product passing a no. 60 and retained on a no. 200 sieve. Analysis showed 11.3 percent of water and 0.4 percent of impurities (iron, etc.). It was prepared for use by heating in the U-tube at 110 to 130 C, in vacuo, for 5 hours. "Potassium Hydroxide" was the U.S.P. material in stick form. Analysis showed 81.9 percent of KOH and 1.3 percent of K_2CO_3. It was crushed to a coarse powder for

[2] Later in the investigation this was replaced by a mercury thermostat.

use. "Aluminum Trioxide" was a commercial product known as "Hydralo". It was similar in form to granular calcium chloride. Analysis showed it to be mainly Al_2O_3 with about 11 percent of water. The U-tube containing the "hydralo" was heated in a bath at 150 to 180 C for 6 hours while passing through it air dried by phosphorus pentoxide. "Calcium Sulphate, Anhydrous (Soluble Anhydrite)" was prepared from the dihydrate $CaSO_4.2H_2O$, which was obtained through the courtesy of James R. Withrow. It was in granular form of 1/10 to 1/20 inch (no. 7 to no. 15 sieve) fineness. The U-tube containing the dihydrate was heated to 220 to 230 C for 2 hours while passing through it air dried by phosphorus pentoxide. The loss in weight indicated that practically all water had been removed. "Calcium Oxide" was the C.P. reagent in powdered form. It was heated to redness (600 to 650 C) for 4 hours and cooled in a desiccator over barium oxide before use. "Magnesium Perchlorate (Anhydrous)", or "Anhydrone" was a commercial product in the form of small lumps of varying size. It was obtained through the courtesy of G. F. Smith. "Barium Oxide" was a specially prepared product obtained through the cooperation of H. S. Booth. It was in a uniformly granular form of 1/10 to 1/20 inch (no. 7 to no. 15 sieve) fineness.

V. ARRANGEMENT OF MATERIALS AND RESULTS OF TESTS

The arrangements of the trains of drying agents in the various tests were as follows, with the material, for which the report is made underlined in each case:

1. $Ba(OH)_2.8H_2O$–$\underline{CuSO_4}$–$Mg(ClO_4)_2.3H_2O$–$Mg(ClO_4)_2$
2. $Ba(OH)_2.8H_2O$–$\underline{CaCl_2}$–(gran.)–NaOH–$Mg(ClO_4)_2.3H_2O$
3. $Ba(OH)_2.8H_2O$—$\underline{CaCl_2}$(tech. anh.)–$CaSO_4$–P_2O_5
4. $Ba(OH)_2.8H_2O$–$\underline{ZnCl_2}$–$Mg(ClO_4)_2.3H_2O$[3]
5. $Ba(OH)_2.8H_2O$–$\underline{Ba(ClO_4)_2}$.[4]–P_2O_5

6a. $Ba(OH)_2.8H_2O$–$\underline{CaCl_2}$ (gran.)—$\underline{NaOH}$–$Mg(ClO_4)_2.3H_2O$–KOH –P_2O_5

6b. $Ba(OH)_2.8H_2O$–$CaCl_2$ (gran.)—$\underline{NaOH}$–KOH–$Mg(ClO_4)_2$

7a. $Ba(OH)_2.8H_2O$–$\underline{CaCl_2}$ (anh.)—$\underline{Mg(ClO_4)_2}$–P_2O_5

7b. $Ba(OH)_2.8H_2O$–$\underline{CaCl_2}$ (anh.)—$CaSO_4$–$Mg(ClO_4)_2$–P_2O_5

8. $Ba(OH)_2.8H_2O$–$\underline{Mg(ClO_4)_2.3H_2O}$–$CaSO_4$–$Mg(ClO_4)_2$–$P_2O_5$

9. $Mg(ClO_4)_2.3H_2O$–$\underline{\text{silica gel}}$–$\underline{Al_2O_3}$–$P_2O_5$

10. $Ba(OH)_2.8H_2O$–$\underline{Mg(ClO_4)_2.3H_2O}$–$\underline{KOH}$–$Mg(ClO_4)_2$[5]

11. $Mg(ClO_4)_2.3H_2O$–silica gel–$\underline{Al_2O_3}$–$\underline{P_2O_5}$

12a. $CaCl_2$(gran.)–silica gel–$\underline{CaSO_4}$–P_2O_5

12b. $Ba(OH)_2.8H_2O$–$\underline{CaSO_4}$–$\underline{P_2O_5}$

13. $CaCl_2$(gran.)–$\underline{CaO}$–$\underline{P_2O_5}$

14a. $Ba(ClO_4)_2$.–$\underline{Mg(ClO_4)_2}$–$\underline{Mg(ClO_4)_2}$–P_2O_5

14b. Al_2O_3–$\underline{Mg(ClO_4)_2}$–P_2O_5

15. $Ba(OH)_2.8H_2O$–$\underline{BaO}$[6]–P_2O_5

Results are summarized in table 1 and shown graphically in figure 2.

[3] Correction made for residual water from $Mg(ClO_4).3H_2O$.
[4] A straight tube 30 cm by 1.75 cm was substituted for the U-tube.
[5] Correction made for residual water from $Mg(ClO_4)_2$.
[6] A straight tube 30 cm by 1.75 cm was substituted for the U-tube.

TABLE 1.—*Results of tests*

Number of tests	Material	Volume of air per hour per ml desiccant (ml)	Total volume of air per ml of desiccant (l)	Residual water per liter of air (mg)	Values from published data (mg/l)
5	$CuSO_4$ (anh.)	36 to 50	0.45 to 0.7	2.8 (2.7 to 2.9)	1.7 at 30 C (7).
4	$CaCl_2$ (gran.)	66 to 165	6.1 to 24.2	1.5 (1.4 to 1.6)	
3	$CaCl_2$ (tech. anh.)	115 to 150	4.0 to 5.8	1.25 (1.23 to 1.27)	
6	$ZnCl_2$ (sticks)	120 to 335	.8 to 2.1	0.98 (0.94 to 1.02)	0.95 at 30 C (4).
2	$Ba(ClO_4)_2$ (anh.)	26 to 36	2.3 to 3.7	0.82 (0.76 to 0.88)	0.29 at 27 C (19).
4	NaOH (sticks)	75 to 170	2.3 to 8.9	0.80 (0.78 to 0.83)	0.16 at 25 C (2).
3	$CaCl_2$ (anh.)	75 to 240	1.2 to 7.8	0.36 (0.33 to 0.38)	
3	$Mg(ClO_4)_2.3H_2O$	65 to 160	4.0 to 7.2	0.031 (0.028 to 0.033)	0.36 at 25 C (3).
4	Silica gel	65 to 135	6.5 to 7.7	0.03 (0.02 to 0.04)	
3	KOH (sticks)	55 to 65	3.2 to 7.2	0.014 (0.010 to 0.017)	0.002 at 25 C (2).
4	Al_2O_3	65 to 135	6.5 to 7.7	0.005 (0.004 to 0.009)	0.003 at 25 (7).
4	$CaSO_4$ (anh.)	75 to 150	1.2 to 18.5	0.005 (0.004 to 0.006)	0.005 at 25 (10).
4	CaO	60 to 90	7.6 to 10.1	0.003 (0.003 to 0.004)	0.2 to 0.3 at 25 C (7).
5	$Mg(ClO_4)_2$ (anh.)	95 to 130	6.4 to 13.2	0.002 (0.002 to 0.003)	(20).
2	BaO	64 to 66	10.6 to 25	0.00065 (0.0006 to 0.0008)	Less than 0.0003 at "ordinary temp." (5).

[1] Numbers in parentheses refer to "References", p. 248.

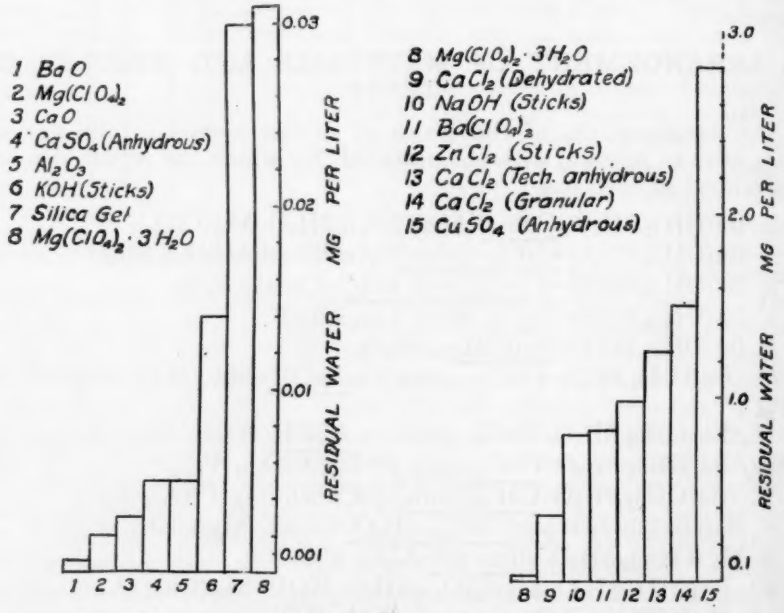

FIGURE 2.—*Graphical representation of comparative efficiencies.*

VI. DISCUSSION OF RESULTS

Previous investigations of the efficiency of dehydrating agents have been made, almost without exception, at one or more of the three temperatures, 0, 25, and 50 C, and therefore comparisons between the results obtained in the present work and those obtained in previous investigations can be made only by estimation. Such comparisons show agreement in some cases but in others there is a marked variation, attributable in the cases of anhydrous copper sulphate, sodium hydroxide, and potassium hydroxide, to the fact that in the

present investigation the regular stock reagents were used, whereas previous investigators used specially prepared materials.

In the case of calcium oxide an efficiency was found which is nearly 100 times as great as that reported in the literature (7). The efficiency will be greatly reduced if it contains even small amounts of silicates and aluminates which melt and form a glaze over the particles when the lime is burned.

The efficiency of "dehydrite" reported in the literature (21) is somewhat lower than was obtained in the present work. This may be largely because of differences in the rate of gas flow.

There has been confusion in the reported efficiency of calcium chloride, largely because of a difference in the materials studied. The equilibrium pressures for the "lowest hydrate" of calcium chloride have been reported to be 0.29 mm, 2.17 mm, and 3.50 mm at 0, 24, and 30 C respectively (6). According to Baxter and Starkweather (2) W. F. Hillebrand called their attention to the fact that these pressures applied to the hydrate containing 26 percent of water. This would correspond to the dihydrate. In the present investigation the granular calcium chloride first studied was approximately the monohydrate with equilibrium pressure of about 1.6 mm at 30.5 C while the equilibrium pressure for anhydrous calcium chloride (the ordinary granular calcium chloride after heating to 260–275 C) is reported to be from 0.14 to 0.25 mm at 25 C (14). The present tests of the anhydrous salt (table 1) indicate a pressure of about 0.38 mm at 30.5 C.

"Anhydrone" is reported as leaving no weighable residual water after passing 210 liters of air through it at 25 C (21). The rate of air flow was 65 to 152 ml per hour per ml of desiccant. In the present investigation, the rate of air flow varied from 95 to 130 ml per hour per ml of desiccant and the volume of air used in the 5 tests varied from 128 to 263 liters. At 30° weighable amounts of residual water were found in all cases.

Barium oxide is reported as leaving less than 0.0003 mg of residual water per liter of gas dried at ordinary temperatures (5). In the present work the amount of residual water at 30.5 C was 0.0005–0.0008 mg. In view of the fact that "ordinary temperatures" may include a temperature as much as 10° lower than that at which the present tests were made, the agreement between results seems fairly good.

"Desicchlora" is reported as leaving 0.29 mg of residual water per liter after drying 198 liters of gas at a rate of 233 ml per hour per ml of desiccant and 0.42 mg of water per liter after drying 110 liters at a rate of 356 ml per hour per ml of desiccant (20). The temperature in both cases was 27 to 27.5 C. The dimensions of the drying column were 30.5 by 2.54 cm. In the present investigation the amount of air dried was 167 liters at a rate of 36 ml per hour per ml of desiccant and 263 liters at a rate of 26 ml per hour per ml of desiccant, leaving 0.88 and 0.76 mg of residual water per liter, respectively. The dimensions of the column of "desicchlora" were approximately 30 by 1.75 cm and the temperature was the same as used throughout, viz, 30.5 C.

Aluminum trioxide is stated in the literature to leave no residual water in gas passed through it at 18 or 20 C until it has taken up 18 percent of its own weight. Another investigator reports 0.003 mg of residual water per liter of air at 25 C (7). The material used in this

investigation, viz, "Hydralo", after a reactivation treatment, was found to have an efficiency in fair agreement with one previously reported (7). Without the preliminary heat treatment the efficiency was very much lower.

This work was done at the suggestion, and under the direction of, E. W. Washburn, chief of the chemistry division of the Bureau of Standards.

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SOME PHYSICAL PROPERTIES OF PLATINUM-RHODIUM ALLOYS

By J. S. Acken [1]

ABSTRACT

In a continuation of the study at the Bureau of the metals of the platinum group, a series of platinum-rhodium alloys containing approximately 10, 20, 40, 60, and 80 percent rhodium was prepared from pure platinum and pure rhodium. The melting point, hardness, density, electrical resistivity, temperature coefficient of resistance, and thermal electromotive force against platinum were determined for each alloy. The microstructure of each alloy appeared to be that of a solid solution. The particular qualifications of the alloys containing 20 to 40 percent of rhodium, for use as resistance furnace windings for service at high temperatures, are discussed.

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I. INTRODUCTION

As part of the study at the Bureau of Standards of the platinum-group metals of high purity, and to supplement the determination of a number of physical properties of pure rhodium, the preparation and properties of platinum-rhodium alloys were given consideration.

Since rhodium is much less abundant than platinum and the alloys high in rhodium are not easily worked, interest in platinum-rhodium alloys has been limited largely to those containing less than 20 percent of rhodium. Alloys containing about 10 percent of rhodium are used as positive elements in thermocouples, as catalytic gauzes for the oxidation of ammonia to nitric acid, and to some extent as the heating element in resistance furnaces. Alloys containing 3 to 4 percent of rhodium are used for crucibles and similar laboratory ware.

Published information on the physical properties of platinum-rhodium alloys is scattered and incomplete. Some of the early work is of doubtful value since reliable methods for the separation, purification, and analysis of the metals of the platinum group were not avail-

[1] With the cooperation of members of the Bureau staff, as indicated by footnote to several sections of this paper.

able until recently. Some of the more important early investigations were those of Le Chatelier,[2] Dewar and Fleming,[3,4] Holborn and Wien,[5] and Barus.[6] Later, when somewhat better methods for purification had been developed, Burgess,[7] Sosman,[8] and Adams[9] studied the use of platinum-rhodium alloys for measuring high temperatures. Subsequently, Neville[10] described in detail a method for the preparation of the 10 percent rhodium alloy of high purity for use in thermocouples.

Data on hardness, tensile strength, electrical resistivity, and temperature coefficients of electrical resistance of platinum-rhodium alloys containing 3.5, 10, 20, and 50 percent of rhodium were presented by Carter;[11] Von Wartenberg[12] determined the melting point of the 10 percent alloy, and Müller[13] the melting points of a series of platinum-rhodium alloys. In the present investigation the "melting point", density, hardness, electrical resistivity, temperature coefficient of electrical resistance, and thermal electromotive force against platinum were determined for a series of alloys which covered the range from pure platinum to pure rhodium.

II. PREPARATION AND MECHANICAL WORKING

The alloys were prepared from platinum and rhodium purified in the Chemistry Division of the Bureau by the methods described by Wichers, Gilchrist, and Swanger.[14] Spectroscopic analysis of the platinum and rhodium showed that the total amount of metallic impurities in each was definitely not over 0.01 percent, probably not over 0.001 percent.

Platinum-rhodium alloys of a nominal rhodium content of 10, 20, 40, 50, 55, 60, and 80 percent, respectively, were prepared in amounts of 50 to 75 grams by melting in a high-frequency induction furnace.[15] For all of the alloys, the constituent metals were prepared in the form of pellets made by compressing the spongy metal and sintering the compressed pellets on a block of lime with an oxy-hydrogen torch. The alloys containing 60 percent or less of rhodium were melted in air in zirconium-oxide crucibles and the 80 percent rhodium alloy in vacuo in a thorium-oxide crucible. The alloys containing 10 and 20 percent of rhodium were cast into graphite molds; the others were allowed to freeze in the crucible. All appeared to be homogeneous.

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[15] The technique of melting, casting, and working these alloys is essentially that described in references 10 and 18.

The ingots were hand forged at 1,100 C (approximate) to bars about 10 mm in diameter. The alloys containing 40 and 80 percent of rhodium were extremely coarse grained in the initial state, i.e., furnace cooled, and were not forgeable. However, after the ingots had been remelted on lime with an oxy-hydrogen flame, they could be forged. Each of the hot-forged bars was swaged to wire about 1 mm in diameter. The 10 percent alloy was swaged at room temperature, the others at 900 to 1,000 C. The 20 percent alloy could be swaged at room temperature if annealed after each reduction.

Further reduction of the 1 mm swaged wires was accomplished by drawing through dies. The alloys containing more than 40 percent of rhodium were drawn hot through tungsten carbide dies until the diameter was reduced to 0.5 mm. The temperature of the wire was maintained at about 900 C for the first few draughts, and then gradually lowered for successive draughts to about 550 C for the draught through the 0.5 mm die. Reduction to 0.2 mm diameter was accomplished by drawing through sapphire dies, at room temperature and without annealing. The alloys containing less than 40 percent of rhodium were drawn at room temperature from 1 mm swaged bar to wire of 0.2 mm diameter.

Determinations of the various physical properties were made during the course of the mechanical working when the form was suitable for specimens for the particular determination desired. Before any determinations were made the specimens were cleaned by immersion in molten potassium bisulphate. This removed surface contamination, especially iron, accumulated during the mechanical working.

The nominal and the actual compositions of the principal alloys, as determined by chemical analysis,[16] are given in table 1. This series of alloys was used for most of the determinations of properties but alloys similar, although of slightly different compositions, were substituted for the 18.7, 37.5, and 77.1 percent alloys in the determinations of temperature coefficient of resistance, resistivity, and density.

TABLE 1.—*Composition of platinum-rhodium alloys*

Nominal		Found by analysis	
Rhodium	Platinum	Rhodium	Platinum
Percent	*Percent*	*Percent*	*Percent*
10	90	10	90
20	80	18.7	81.3
40	60	37.5	62.5
50	50	51.6	48.4
55	45	56.6	43.4
60	40	61.2	38.8
80	20	77.1	22.9

[16] The analyses were made by Raleigh Gilchrist, Associate Chemist. Ignition at dull-red heat with sodium chloride in an atmosphere of chlorine was used in getting the alloys, particularly those high in rhodium, into solution. The details of the method of analysis are described in a pending paper.

III. PHYSICAL PROPERTIES

1. MELTING POINT

Determinations were made of the approximate "melting point" of each of the alloys containing 10, 18.7, 37.5, 56.6, and 77.1 percent of rhodium. Platinum and rhodium are generally believed to form a continuous series of solid solutions and the melting or freezing in each case occurs over a range of temperature rather than at a single temperature.

The apparatus and procedure were similar to those used in previously reported determinations of the melting points of high-purity platinum and rhodium.[17] [18] An ingot (50 to 75 g) of the alloy with a hole drilled axially from top to bottom was placed in a thorium-oxide crucible fitted with a thorium-oxide sight-tube which was inserted

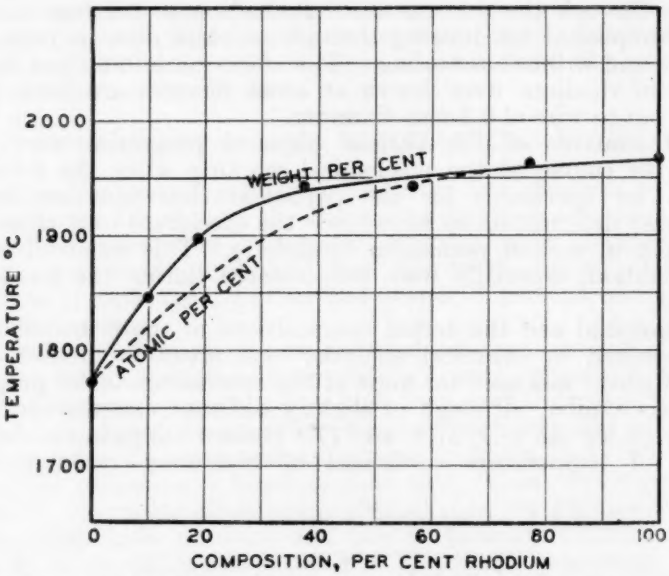

FIGURE 1.—*"Melting Points" of alloys of platinum and rhodium.*

in the hole. The power input to the high-frequency induction furnace which was used for melting the ingot was controlled so that several observations of the temperature could be made during melting or freezing. The alloys containing 40 percent or less of rhodium were melted in air; those of higher rhodium content in an evacuated furnace tube, under pressure of less than 1 mm of mercury.

Temperatures were measured with a Leeds and Northrup optical pyrometer which was calibrated by the pyrometry section of the Bureau before the observations were made and again after they had been completed. The calibration of this pyrometer was certified to ±20 C for temperatures between 1,700 and 2,000 C. Consequently the accuracy of the temperature observations cannot exceed the accuracy, ±20 C, of the pyrometer calibration.

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In each of the time-temperature curves summarizing the observations during melting and freezing of the different alloys only one break was detected instead of the two that might be expected at the solidus and liquidus temperatures of a solid-solution alloy. In every case, the break was pronounced, and temperatures that were constant, within the uncertainty to which they are given, were obtained both on melting and on freezing over periods of from 2 to 5 minutes. For each of the alloys there was close agreement between the temperatures at which melting and freezing occurred, which indicates that the range between the solidus and liquidus temperatures is probably small. Evidently, at the high temperatures at which the observations were made, the change in the rates of heating or cooling at the solidus and liquidus temperatures was too slight to be detected with the optical pyrometer and the procedure employed.

TABLE 2.—*"Melting points" of platinum-rhodium alloys*

Composition		Arrest on heating	Arrest on cooling	"Melting point" [a]
Rhodium (percent)	Platinum (percent)	°C	°C	°C
10	90	1,848 1,845 1,845	1,845 1,851 1,845	1,845±20
Average		1,846	1,847	
18.7	81.3	1,899 1,906 1,889 1,906	1,890 1,905 1,880 1,899	1,900±20
Average		1,900	1,894	
37.5	62.5	1,940 1,946 1,951 1,949 1,943	1,953 1,942 1,933 1,942 1,930	1,945±20
Average		1,946	1,940	
56.6	43.4	1,955 1,946 1,934 1,948	1,936 1,938 1,933 1,945	1,940±20
Average		1,946	1,938	
77.1	22.9	1,962 1,965 1,957 1,967	1,964 1,963 1,965 1,954	1,960±20
Average		1,963	1,961	

[a] The limit of accuracy (±20C) ascribed to each "melting point" is the limit of accuracy of the pyrometer calibration.

From 3 to 5 sets of temperature observations were made during melting and during freezing of each of the alloys. The temperatures during the period in which they remained constant (while melting or freezing occurred) are given in table 2. The data show that the precision of the experimental results is well within the limits of accuracy of the pyrometer calibration. The average of the arrests during heating and cooling of each alloy, rounded off to the nearest 5 C, is designated as the "melting point." Actually this temperature is

somewhere between the solidus and the liquidus temperatures. In figure 1, the "melting points" are summarized for the various platinum-rhodium alloys, together with the melting (or freezing) points of platinum 1,773.5 C,[19] and of rhodium, 1,966 C.[20] The melting

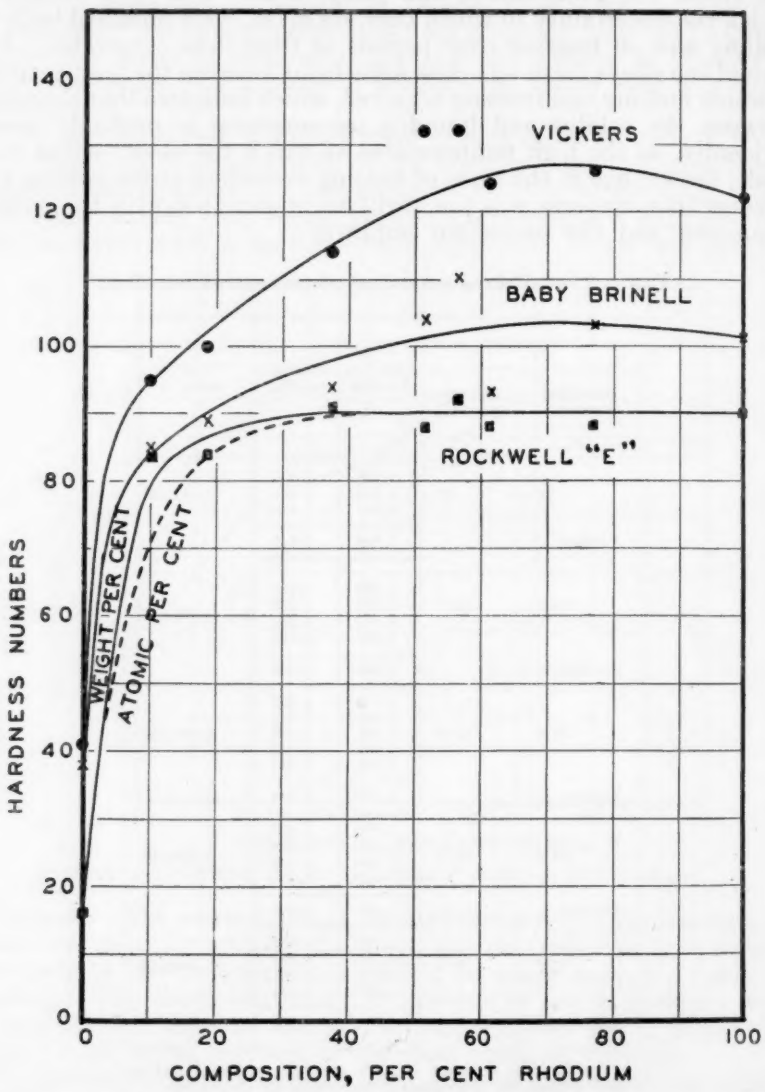


FIGURE 2.—*Hardness of platinum-rhodium alloys.*

points of all the alloys lie between those of pure platinum and pure rhodium. When plotted on the basis of weight percent, the melting point curve rises sharply from the melting point of pure platinum as the rhodium content is increased to about 40 percent. Further increase in the rhodium content, however, is accompanied by rela-

[19] See footnote [17] p. 252.
[20] Determination by W. F. Roeser and H. T. to be Wensel, published subsequently in this journal.

tively small increases in melting point. If the results are expressed in atomic percent, a smoother curve is obtained and the rapid increase in melting point with additions of rhodium up to 40 percent, is less apparent.

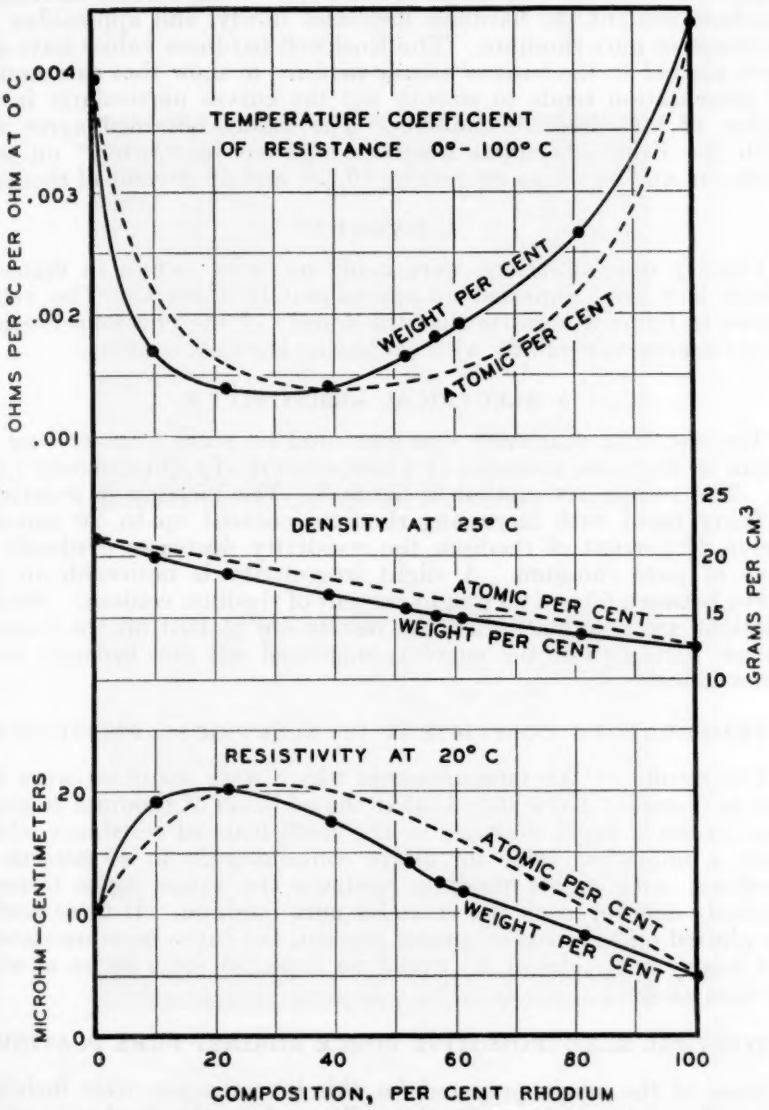


FIGURE 3.—*Density, electrical resistivity, and temperature coefficient of resistance of platinum-rhodium alloys.*

2. HARDNESS

The hardness was determined by means of the Baby Brinell, Rockwell, and Vickers hardness testers. The ingots previously used for the melting point determinations were hot forged to square bars and annealed at 1,200 C before the hardness impressions were made.

The results on a weight percent basis are shown graphically in figure 2. The 10 percent rhodium alloy is decidedly harder than pure platinum. With increased rhodium contents above 10 percent the hardness increases at a slower rate, and apparently reaches a maximum at about 70 percent of rhodium. With further increase in rhodium content the hardness decreases slowly, and approaches the hardness of pure rhodium. The Rockwell hardness values have also been plotted on the basis of atomic percent, to show that this method of presentation tends to smooth out the curves particularly in the region of low rhodium contents. The values obtained agree well with the Brinell hardness numbers reported by Carter,[21] on pure platinum and on alloys containing 10, 20, and 50 percent of rhodium.

3. DENSITY [22]

Density determinations were made on wires 1 mm in diameter which had been annealed at approximately 1,500 C. The values shown in figure 3 indicate that the density of the platinum-rhodium alloys decreases regularly with increasing rhodium content.

4. ELECTRICAL RESISTIVITY [23]

The electrical resistivity was measured on wires 1 meter long by 1 mm in diameter, annealed at a temperature of approximately 1,500 C. The results are plotted in figure 3. The increase in resistivity is fairly rapid with increasing rhodium content up to 20 percent; above 20 percent of rhodium the resistivity decreases gradually to that of pure rhodium. A slight irregularity is noticeable in the curve between 50 and 60 weight percent of rhodium content. Similar relations are apparent when the results are plotted on the basis of atomic percent, but the curve is smoothed out and becomes more symmetrical.

5. TEMPERATURE COEFFICIENT OF ELECTRICAL RESISTANCE [24]

The results of the measurements which were made on wires 0.2 mm in diameter, show (fig. 3) that the addition of rhodium to platinum causes a rapid decrease in the coefficients of resistance which reach a minimum value for alloys containing 20 to 40 percent of rhodium; with higher rhodium contents the values again increase regularly and approach the value for pure rhodium. If these results are plotted on the basis of atomic percent, the curve becomes smooth and nearly symmetrical, as would be expected for a series of solid solution alloys.

6. THERMAL ELECTROMOTIVE FORCE AGAINST PURE PLATINUM

Some of the alloys prepared for this investigation were included in a series of 10 platinum-rhodium alloys whose thermoelectric properties over the temperature range 100 to 1,200 C have already been published.[25]

[21] See footnote 11, p. 250.
[22] E. L. Peffer, Chief, section of capacity and density.
[23] A. R. Lindberg, junior electrical engineer, section of electrical resistance.
[24] F. R. Caldwell, Assistant Physicist, pyrometry section.
[25] Frank R. Caldwell, Thermoelectric Properties of Platinum-Rhodium Alloys. B. S. Jour. Research, vol. 10, pp. 373-380, 1933.

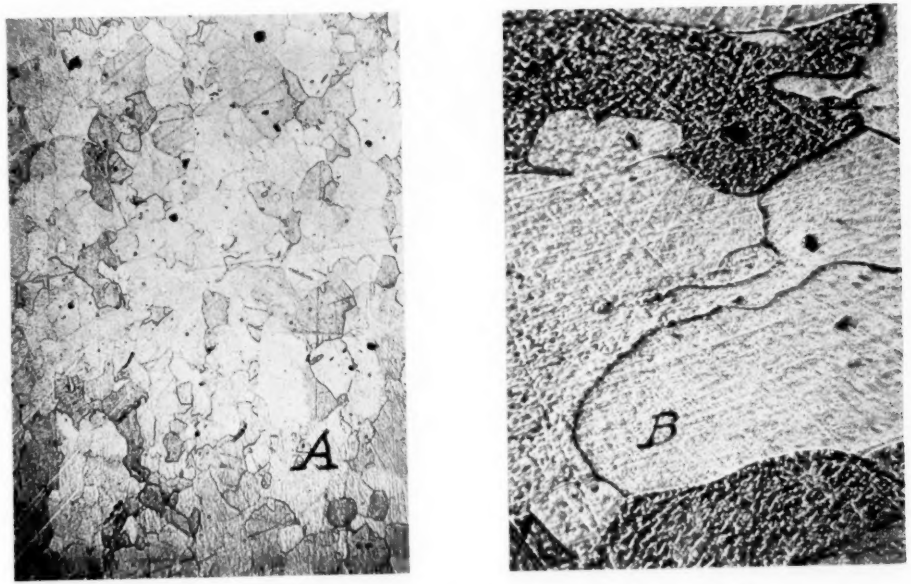


FIGURE 4.—*Microstructure of the 37.5 percent rhodium alloy.*

This is typical of the platinum-rhodium alloys. Etched by immersion in molten potassium pyrosulphate. Magnification, A, × 100; B, × 500.

UNIV. OF MICH.

7. STRUCTURE OF PLATINUM-RHODIUM ALLOYS [26]

Two previous investigators [27] have stated that platinum and rhodium form a continuous series of solid solutions. In the present investigation, slight irregularities in melting point, Brinell hardness, electrical resistivity, and thermoelectric force of the alloys containing about 55 percent of rhodium suggested the possibility that there might be some departure from a simple solid solution at or near this composition. The presence of impurities, to account for these irregularities, could not be established by chemical and spectrographic analyses.

Examination of the microstructure failed to reveal evidence of any phase except a solid solution in any of the alloys used in this investigation. The specimens used for the microscopic examination were swaged wires, 1 mm in diameter, which had been annealed at 1,500 C. Figure 4 shows the microstructure of the alloy containing 37.5 percent of rhodium. This was typical of the structure of the other alloys of the series.

X-ray diffraction patterns made from filings of each of the alloys likewise failed to reveal any significant difference in structure to account for the irregularity in properties of some of the alloys. Evidence of the existence of phases other than a simple solid solution was not obtained.

IV. DISCUSSION

When the technic for the production of rhodium wire was developed [28] it became possible to use rhodium or platinum-rhodium alloys of high rhodium content for windings on furnaces which were to be operated at temperatures higher than could be reached with platinum. Pure rhodium and an alloy containing 80 percent of rhodium and 20 percent of platinum have been successfully used at this Bureau to maintain furnace temperatures above the melting point of platinum. However, the melting point curve shows that but little advantage can be gained by using alloys containing more than 40 or 50 percent of rhodium. The 40 percent alloy is much easier to work than the 80 percent alloy or pure rhodium and hence should be cheaper, at least at present prices for rhodium and platinum. It also has greater resistivity and a lower temperature coefficient of resistance (both measured at ordinary temperatures) than the alloy of higher rhodium content.

[26] R. E. Pollard and R. G. Kennedy, Jr., Junior Metallurgist and Assistant Metallurgist, respectively.
[27] See footnotes 11 and 13, p. 250.
[28] See footnote 18, p. 250.

It will be noted that the temperature coefficient of resistance is at a minimum for alloys containing 20 to 40 percent of rhodium and that the resistivity is at its maximum between 10 and 40 percent. In these respects an alloy containing about 20 percent of rhodium is evidently superior to the ordinary platinum winding. Such an alloy can be drawn into wire nearly as easily as platinum and weighs about 15 percent less per unit length. Observations of the 10 and 20 percent alloys in service indicate that they deteriorate less rapidly than platinum, under comparable conditions. For all these reasons they are preferable to platinum for use in furnace windings as long as the cost of rhodium does not rise very much above that of platinum. Only the requirement of a higher operating temperature would appear to justify the use of the less easily worked alloys of higher rhodium content.

WASHINGTON, November 10, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP651

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

A FRACTIONATING COLUMN WITH FRITTED GLASS PLATES [1]

By S. T. Schicktanz [2]

ABSTRACT

This paper describes a fractionating column with fritted glass plates which has a higher plate efficiency than the usual laboratory bubble-cap column. The efficiency of this type of plate is approximately 98 percent as compared to 87 percent for the bubble-cap plate.

In a previous paper [3] describing fractionating columns, it was shown that the plate efficiency for the laboratory type of bubble-cap still is only 87 percent. The deficiency of 13 percent is probably due to the large bubbles which are formed on the plates by the large slots in the bubble caps. The efficiency can be increased either by lengthening the time of contact between vapor and liquid or by reducing the size of the bubbles. The time of contact between vapor and liquid can be lengthened only by increasing the height of liquid held on each plate or decreasing the velocity of the vapor and the output of the column. Both alternatives have disadvantages. By increasing the surface of contact between the vapor and liquid through a reduction in the size of the bubbles and by keeping the hold-up of the column and the rate of distillation constant, it is possible to increase the efficiency of the plate.

The Fish-Schurman Corporation [4] furnished us with fritted glass disks of different porosities which were tested for operative efficiency. The Jena Glass Works of Schott and Genossen constructed a still made entirely of Jena's low coefficient of expansion glass G-20 and made it available to the Bureau. The plates having the finest pores gave the smallest bubbles but developed too great a back pressure. After testing plates of several porosities, those designated by the manufacturer as no. "O" were selected for use in the construction of the experimental still containing five plates.

The design of the column is the same as previously described except that the bubble plate is replaced by a fritted disk, and the liquid overflow, through the side tube, is placed only 1 cm above the top of the plate. This change keeps the hold-up of the plate equal to that for the bubble cap, although it decreases the height of liquid through which the vapor must pass.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of project no. 6; The separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research associate representing the American Petroleum Institute at the Bureau of Standards.

[3] Laboratory rectifying stills of glass by Johannes H. Bruun and Sylvester T. Schicktanz, B. S. Jour. Research, vol. 7, p. 852, 1931.

[4] 230 East Forty-fifth Street, New York, N.Y.

The efficiency tests were made with the usual test mixture containing 50 mole percent each of ethylene chloride (B.P. 83.7 C) and benzene (B.P. 80.2 C). Figure 1 shows the effective separation of the two components when using a reflux ratio of 20:1; a rate of collection of the distillate of 1 ml per minute, and keeping the column as well insulated as possible by means of suitable lagging.

The plate efficiencies were determined by the method of McCabe and Thiele.[5] In this method the distillation is interrupted at a certain stage and the composition of the distillate and the liquid remaining in the pot are determined. From the reflux ratio and the vapor-liquid diagram of the mixture of these substances, it is possible to obtain an approximate theoretical number of plates which should give the separation shown by the composition of the distillate and pot liquid. This theoretical number of plates, divided by the actual number of plates used and multiplied by 100, gives the plate efficiency of the still in percentage. Table 1 shows the plate efficiency as determined during the test run.

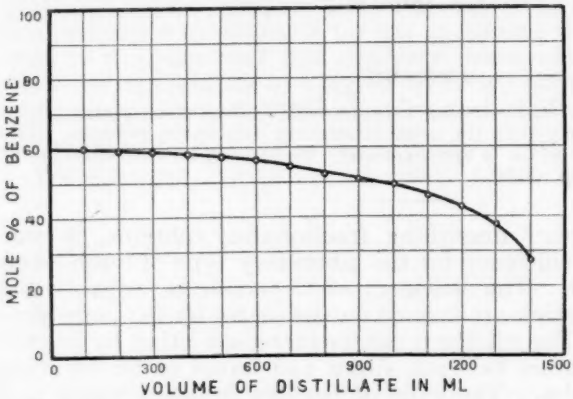


FIGURE 1.—*Efficiency curve for a fritted glass plate column containing 5 plates.*

Ordinate: Mole percent of benzene in the distillate.
Abscissa: Total volume of distillate collected.

TABLE 1.—*Plate efficiencies of a fritted glass plate column*

Percentage of charge distilled	Composition of fraction (mole percent benzene)	Composition of pot residue (mole percent benzene)	Theoretical number of plates	Plate efficiency percent
				Percent
33.3	59.9	45.3	4.94	98.46
53.3	55.1	40.5	4.91	98.3
63.3	52.9	38.3	4.93	98.7
86.6	40.6	26.2	5	100

These values for the plate efficiency are only approximate and depend to a large extent on the reflux ratio. In a test with an unlagged column, the calculated efficiency was as high as 108 percent, showing that there was a greater reflux ratio throughout the column than was assumed to be present.

This type of still decreases the "H.E.T.P." (height equivalent to a theoretical plate) and is very useful where the height of the room is an essential factor in limiting the effectiveness of a column.

[5] W. L. McCabe and E. W. Thiele, Ind. Eng. Chem., vol. 17, p. 605, 1925.

Because of the small porosity of the plates, the liquid will remain on the plates when the distillation is stopped and will not drain down the column unless the back pressure is decreased too much by condensation of the vapors in the pot and the column.

Although this still is not as efficient as some packed column stills [6] of the same dimensions, it is more generally useful since corrosive liquids can be readily fractionated without harmful effects to either the liquid or column.

WASHINGTON, November 23, 1933.

[6] See Note on an Improved Chain-Packed Distilling Column, S. T. Schicktanz, B.S., Jour. Research, vol. 11, p. 89, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP652

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

FILTERS FOR PRODUCING THE COLOR OF THE EQUAL-ENERGY STIMULUS

By Raymond Davis and K. S. Gibson

ABSTRACT

Two filters have been prepared similar to other Davis-Gibson filters, which when combined with an illuminant at 2848 K give the color of the so-called equal-energy stimulus. One of these has been designed on the basis of the O.S.A. observer, the other on the basis of the I.C.I. observer. Spectrophotometric and colorimetric data are given.

So far as known, but one attempt has been made to produce accurately the color of the so-called equal-energy stimulus, i.e., the color of an hypothetical illuminant whose spectral energy per unit wave length is equal in amount at all wave lengths. A combination glass filter was designed by one of the authors in 1926 [1] which, when used with Abbot-Priest sunlight [2] gave by computation a chromaticity match with the equal-energy stimulus. The resulting equal-energy color was used by Priest in "An Experiment Bearing on the Adoption of a Standard Neutral Stimulus in Colorimetry: The Choice as Between 'Sun' and 'Equal Energy'." [3]

This experiment illustrates one of the uses of an illuminant having the color of the equal-energy stimulus. Such an illuminant would also be useful as the heterogeneous stimulus in experimental determinations of dominant wave length and purity, the equal-energy stimulus having been adopted as the basic stimulus in the 1931 I.C.I. coordinate system.[4]

The present filters have been designed in order to make the color of the equal-energy stimulus readily available. Except for the necessary variations in composition they are identical with other Davis-Gibson filters.[5] Readers are referred to B.S. Misc. Pub. No. 114 regarding selection of materials, preparation of solutions, and the filling of cells, and for general spectrophotometric and colorimetric data on the filter components.

Spectrophotometric and colorimetric data on these filters and on the resulting energy distributions are given in the accompanying figures and table. Figure 1 is a chart, similar to those of B.S. Misc. Pub. No. 114, which gives the spectral transmission [6] of the filter, the resulting

[1] K. S. Gibson, The Production of Radiant Energy of Uniform Intensity Over the Visible Spectrum, Jour. Opt. Soc. Am. and Rev. Sci. Insts., vol. 13, p. 305, 1926.

[2] Irwin G. Priest, Standard Artificial Sunlight for Colorimetric Purposes, Jour. Opt. Soc. Am. and Rev. Sci. Insts., vol. 12, p. 479, 1926.

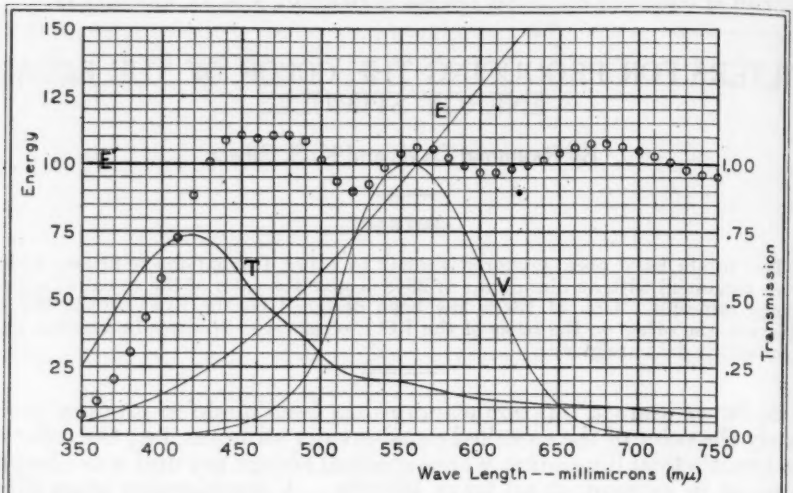
[3] Jour. Opt. Soc. Am. and Rev. Sci. Insts., vol. 13, p. 306, 1926.

[4] Deane B. Judd, The 1931 I.C.I. Standard Observer and Coordinate System, Jour. Opt. Soc. Am., vol. 23, pp. 359-374, 1933. See footnote 12 of Judd's paper.

[5] Raymond Davis and K. S. Gibson, Filters for the Reproduction of Sunlight and Daylight and the Determination of Color Temperature, B.S. Misc. Pub. no. 114, 1931. Copy may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D.C., at 45 cents.

[6] Derived from the standard data on the filter components.

2848°K TO EQUAL ENERGY CHART 39



λ (mμ)	T	E''*	E''/E'
350	0.259	7.0	.070
60	.351	12.3	.123
70	.449	20.0	.200
80	.543	30.3	.303
90	.626	43.2	.432
400	.684	57.4	.574
10	.721	72.7	.727
20	.736	88.2	.882
30	.716	100.7	1.007
40	.663	108.6	1.086
450	.585	110.6	1.106
60	.508	109.6	1.096
70	.451	110.3	1.103
80	.402	110.7	1.107
90	.353	108.5	1.085
500	.297	101.4	1.014
10	.248	93.5	.935
20	.217	89.9	.899
30	.205	92.6	.926
40	.201	98.5	.985
550	.196	103.8	1.038
60	.186	106.1	1.061
70	.172	105.2	1.052
80	.156	102.2	1.022
90	.1426	99.1	.991
600	.1316	96.8	.968
10	.1244	96.8	.968
20	.1195	97.9	.979
30	.1156	99.4	.994
40	.1121	101.1	1.011
650	.1103	103.8	1.038
60	.1080	106.0	1.060
70	.1051	107.2	1.072
80	.1016	107.5	1.075
90	.0969	106.2	1.062
700	.0926	104.8	1.048
10	.0881	102.8	1.028
20	.0834	100.2	1.002

Bureau of Standards. Davis-Gibson Filters

T--Spectral Transmission of Filter
V--Relative Visibility Function
E--Relative Energy of 2848°K
E'--Equal Energy

E''(=T×E)*----Relative Energy of 2848°K and Filter Combination

Light Transmission of Filter for 2848°K = 0.174 **

FILTER FORMULA

A

Copper Sulphate ($CuSO_4 \cdot 5H_2O$)	3.134	grams
Mannite ($C_6H_8(OH)_6$)	3.134	grams
Pyridine (C_5H_5N)	30.0	cc
Water (distilled) to make	1000.	cc

B

Cobalt Ammonium Sulphate ($CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$)	31.180	grams
Copper Sulphate ($CuSO_4 \cdot 5H_2O$)	17.154	grams
Sulphuric Acid (sp. gr. 1.835)	10.0	cc
Water (distilled) to make	1000.	cc

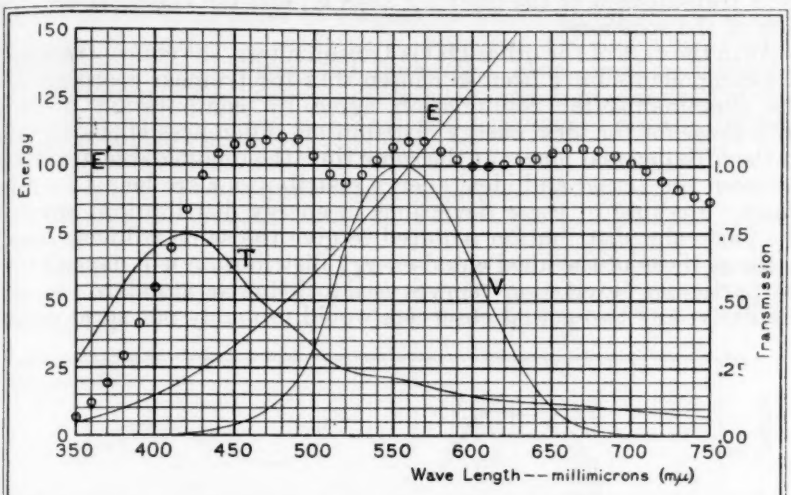
These data are for a one centimeter layer each of solutions A and B in a double cell with three plates of borosilicate crown glass (refractive index, D line, = 1.51), each 2.5 mm thick.

* Adjusted to make sum of E'' - E' from 400 to 720 mμ equal practically to zero

** Factor to be used to multiply the candle-power of the light source to obtain the candle-power of the source-and-filter combination

FIGURE 1.—*Equal-energy filter derived on the basis of the O.S.A. standard observer. This chart is numbered 39 to follow in sequence chart no. 38 of B.S. Misc. Pub. No. 114.*

2848° K TO EQUAL ENERGY I.C.I. OBSERVER



λ (mμ)	T	E''*	E''/E'
350	0.270	6.9	.069
60	.363	11.9	.119
70	.460	19.2	.192
80	.553	29.0	.290
90	.636	41.1	.411
400	.693	54.5	.545
10	.730	69.0	.690
20	.747	83.8	.838
30	.728	96.0	.960
40	.679	104.2	1.042
450	.607	107.3	1.073
60	.533	107.7	1.077
70	.478	109.4	1.094
80	.430	110.8	1.108
90	.380	109.5	1.095
500	.324	103.6	1.036
10	.274	96.7	.967
20	.242	93.6	.936
30	.228	96.3	.963
40	.222	101.9	1.019
550	.215	106.9	1.069
60	.204	108.9	1.089
70	.189	108.0	1.080
80	.172	105.1	1.051
90	.157	102.1	1.021
600	.1449	99.9	.999
10	.1370	99.8	.998
20	.1312	100.7	1.007
30	.1264	101.8	1.018
40	.1220	102.9	1.029
650	.1190	104.9	1.049
60	.1157	106.3	1.063
70	.1114	106.4	1.064
80	.1067	105.7	1.057
90	.1007	103.3	1.033
700	.0952	100.9	1.009
10	.0897	98.0	.980
20	.0841	94.5	.945

Bureau of Standards. Davis-Gibson Filters

T -- Spectral Transmission of Filter
V -- Relative Visibility Function
E -- Relative Energy of 2848° K
E' -- Equal Energy
E'' (=T x E)* ---- -- Relative Energy of 2848° K and Filter Combination

Light Transmission of Filter for 2848° K = 0.191 **

FILTER FORMULA

A

Copper Sulphate ($CuSO_4 \cdot 5H_2O$)	2.954	grams
Mannite ($C_6H_8(OH)_6$)	2.954	grams
Pyridine (C_5H_5N)	30.0	cc
Water (distilled) to make	1000.	cc

B

Cobalt Ammonium Sulphate ($CoSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$)	28.440	grams
Copper Sulphate ($CuSO_4 \cdot 5H_2O$)	17.840	grams
Sulphuric Acid (sp. gr. 1.835)	10.0	cc
Water (distilled) to make	1000.	cc

These data are for a one centimeter layer each of solutions A and B in a double cell with three plates of borosilicate crown glass (refractive index, D line, = 1.51), each 2.5 mm thick.

* Adjusted to make sum of E'' - E' from 400 to 720 mμ equal practically to zero

** Factor to be used to multiply the candle-power of the light source to obtain the candle-power of the source-and-filter combination

FIGURE 2.—*Equal-energy filter derived on the basis of the 1931 I.C.I. standard observer.*

energy distribution when in combination with a 2848 K illuminant, the light transmission of the filter for 2848 K, and the chemical composition of the solutions.

As in the case of the other Davis-Gibson filters, the concentrations of the components have been so chosen that the trilinear coordinates of the illuminant-filter combination agree by computation precisely with those for the ideal energy distribution, differences appearing only in the fifth decimal place; at the same time the unavoidable deviations between the actual and ideal energy distributions are held to a minimum. Because of these deviations in energy distribution, however, the particular distribution required to give the same trilinear coordinates as those of the ideal equal-energy distribution will depend upon the particular "excitation" curves used to define the standard observer. Similarly, any two actual observers would probably not agree exactly

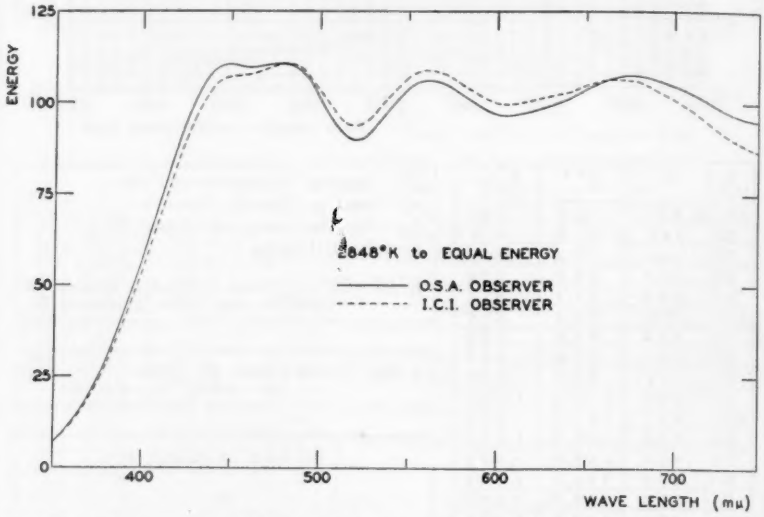


FIGURE 3.—*Comparison of the spectral energy distributions obtained with the two equal-energy filters illustrated in figures 1 and 2.*

as to the degree of chromaticity match given by the ideal and actual stimuli, if both were available for observation.

The filter described in figure 1 was designed on the basis of the O.S.A. standard observer, in terms of which all the filters of B.S. Misc. Pub. No. 114 were designed. A similar filter has also been prepared on the basis of the 1931 I.C.I. standard observer; a chart giving the composition and characteristics of this filter is given in figure 2. The two energy distributions are shown together for comparison in figure 3.

The colorimetric differences resulting from these two distributions are shown in table 1. It is apparent from these data that the filter designed on the I.C.I. basis is slightly yellowish green relative to the filter designed on the O.S.A. basis when both are combined with 2848 K. The chromaticity difference is readily perceptible in a good photometric field but is hardly perceptible when the two filters are merely viewed side by side. The difference is equivalent to approximately two thirds of a Jones hue step, to approximately 10 micro-reciprocal-degrees, or to a Lovibond yellow glass of value N-0.16. It

is thus very small, but might not be negligible for all purposes. Differences of the same order of magnitude would be expected between the filters of series II of B.S. Misc. Pub. No. 114 and similar filters designed on the basis of the I.C.I. observer. Much smaller differences would be found in a similar comparison for the filters of series I of that publication because of the notably better agreement between the ideal and actual spectral energy distributions.

TABLE 1.—*Colorimetric characteristics of equal-energy filters*

Colorimetric quantity	Ideal equal-energy stimulus	Illuminant 2848 K combined with—		Differences O.S.A. minus I.C.I.
		O.S.A. filter	I.C.I. filter	
O.S.A. coordinates: [1]				
r	0.3142	0.3142	0.3206	−0.0064
g	.3062	.3062	.3125	−.0063
b	.3796	.3796	.3669	+.0127
I.C.I. coordinates: [2]				
x	.3333	.3301	.3333	−.0032
y	.3333	.3264	.3333	−.0069
z	.3333	.3435	.3333	+.0102
Correlated color temperature [3], θ_i		5356 K	5271 K	+85 K
Color departure,[3] σ/δ		10.1	5.8	
Conjunctive wave length [3], λ_i, equal energy to black body		565.7 mμ	566.1 mμ	
Conjunctive wave length [3], O.S.A. to I.C.I.		572.0 mμ		

[1] Values of r, g, b computed on basis of O.S.A. excitation curves with Davis-Gibson mean sun as basic stimulus; see reference 5, figure 12.

[2] Values of x, y, z computed on basis of 1931 I.C.I. standard observer and coordinate system with equal energy as basic stimulus; see reference 4, table 3.

[3] Definitions of these terms and description of the methods of computation are given in a paper by Raymond Davis, A Correlated Color Temperature for Illuminants, B.S. Jour. Research, vol. 7 (RP365), pp. 659-681, 1931. It should be mentioned that the I.C.I. data on the r, y and z coordinate system cannot be used to compute correlated color temperature, color departure and conjunctive wave length by the method described in Research Paper No. 365.

WASHINGTON, December 11, 1933.